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DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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All applications for regular or for associate membership in the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio, or to the Office of Publication, 1500 Greenmount Ave., Baltimore, Maryland.

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CHARLES RUDISEL PARK

Charles Rudisel Park, in charge of the Bulletproof Tank Division of The Firestone Tire & Rubber Company, Akron, Ohio, was fatally injured, December 11, 1941, in an explosion in the Parkway Restaurant, near the Firestone plants. He died in a local hospital several hours later.

Mr. Park was born in Tiffin, Ohio, August 21, 1894, and attended grammar school (1900-1908) and high school (1908-1912) in that city. He later attended Heidelberg College and Cornell University, receiving the A.B. degree from the latter institution in 1916. After doing graduate work and serving as assistant in chemistry at the University of Minnesota (1916-1917), he was instructor at the Massachusetts Institute of Technology from 1917 to August 1922. He then joined the research staff of the Goodyear Tire & Rubber Company in Akron. He was engaged in development work on carbon black for the Delano Land Company from 1926 to 1928, and returned to do research work at Goodyear in 1928. From 1930 to 1931 he was chief chemist of the United Carbon Company, and then became a member of the research staff of The Firestone Tire & Rubber Company, where he held the positions of research chemist, head of the division of physical chemical research, and assistant director of research. He became manager of the New Products Division on March 1, 1938, and was placed in charge of the Bulletproof Tank Division on June 1, 1941, in which capacity he was serving at the time of his death. He was the author of publications on the physical properties of rubber compounds, the effects of powders on the reinforcement of rubber, and temperature effects during vulcanization.

Mr. Park was a member of the American Chemical Society (1917), and served the Akron Section as secretary, chairman, and councilor. He was a member also of the American Institute of Chemical Engineers, the American Institute of Chemists, and Alpha Chi Sigma Fraternity. His hobbies were gardening and music. He was active in the civic affairs of his community, and was a member of the City Council of Silver Lake, Ohio. He was a member of the Akron Torch Club and the Akron Friends of Music.

He is survived by his wife, Kathryn, one son, John, age 15, of Silver Lake, Ohio, and his mother and sister, of Tiffin, Ohio.

NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY: 1940. Edited by T. J. Drakeley. Published by the Institution of the Rubber Industry, 12 Whitehall, London, S.W. 1, England. $7\frac{1}{4} \times 9\frac{3}{4}$ in. 160 pp. Price to Members: 2/6; price to Nonmembers: 10/6. Customs duty extra on American copies.

(Available in U. S. from Book Dept., The Rubber Age)

It is a tribute to the entire British rubber industry in general and to the Institution of the Rubber Industry in particular, that this latest report on the progress of rubber technology, the fourth to be issued, has not only made its appearance but made it close to the expected publication date. Like previous issues, reviews in specific fields have been placed in the hands of competent experts in those fields. Complete bibliographical references are given at the end of each chapter. There are 24 chapters in all, plus author and subject indexes. The titles of the chapters and the authors of each follow:

Historical and Statistical Review, T. R. Dawson; *Planting and Production of Raw Rubber and Latex, Gutta-Percha, Balata, Chicle and Jelutong*, T. R. Dawson; *Properties, Applications and Utilization of Latex, Including Treatment of Fabric with Latex*, C. F. Flint; *Chemistry and Physics of Raw Rubber and Rubber Derivatives, Gutta-Percha, Chicle, Balata and Jelutong*, W. J. S. Naunton; *Synthetic Rubber*, Maldwyn Jones; *Testing Equipment and Specifications Other Than for Latex*, W. J. S. Naunton; *Compounding Ingredients, Accelerators, Anti-oxidants and Softeners*, F. H. Cotton; *Fibres and Textiles*, W. Knight; *Chemical and Physical Properties of Vulcanized Rubber*, A. E. T. Neale; *Tires*, J. G. Mackay; *Belting*, G. F. Payne. *Hose and Tubing*, J. Kirkwood; *Cables and Electrical Insulation*, H. A. Daynes; *Footwear*, R. C. Davies; *Games, Sports Accessories and Toys*, J. P. Griffiths; *Mechanical Rubber Goods*, Herbert Rogers; *Roads*, G. E. Coombs; *Flooring*, J. Kirkwood; *Surgical Goods*, C. R. Pinnell; *Textile-Rubber Composites, Solvents, Rubber Composites*, W. N. Lister; *Sponge Rubber*, J. D. Campbell; *Hard Rubber*, B. L. Davies; *Works Processes, Materials, Including the Treatment of Raw Rubber in the Factory, and the Treatment of Vulcanized Rubber*, F. H. Cotton; *Machinery and Appliances*, E. Morris. [From *The Rubber Age* of New York.]

RUBBER RED BOOK. Published by *The Rubber Age*, 250 W. 57th St., New York, N. Y. Cloth, 6 by 9 inches, 512 pages. Price, \$5.

Issued biennially, this directory of the rubber industry and its suppliers has been revised, enlarged, and brought up to date. A new section, accessories and fittings, has been added; while the data formerly included in a section on "Miscellaneous Types of Rubber and Allied Materials" are now presented more completely in new sections on "Rubber Derivatives" and "Synthetic Rubbers and Rubber-Like Materials" and in the section on crude rubber, now expanded to include "related materials." The number of pages has been increased from 422 to 512.

The 1941 edition, besides incorporating revisions and additions, includes sections on: rubber manufacturers in the United States classified alphabetically and according to product and geographical location; Canadian rubber manufacturers; rubber machinery and equipment; rubber chemicals and compounding ingredients; fabrics and textiles; reclaimed rubber; scrap-rubber dealers; rubber latex; miscellaneous products and services; consulting technologists; manufacturers' representatives, sales agents, branch offices, etc.; technical journals; trade and technical organizations; and "Who's Who in the Rubber Industry".

This volume, which compiles and correlates an extensive amount of data, continues as a complete and convenient directory for this field. [From the *India Rubber World*.]

RUBBER. United States Tariff Commission, Washington, D. C. 6 x 9 in. 16 pp.

The possibilities of producing rubber in the United States and those of rubber conservation are detailed in this booklet, issued in the nature of a report. Data on the current status of reclaimed rubber, synthetic rubber and guayule are given. Methods of increasing the production of all three of these materials are discussed. The booklet represents an up-to-date report on the situation confronting the domestic rubber manufacturing industry at present. [From *The Rubber Age* of New York.]

THE RUBBER INDUSTRY. Josephine Perry. Published by Longmans, Green & Co., New York, N. Y. 1941. Cloth, 6½ by 8¼ inches, 96 pages. Indexed. Price \$1.50.

Written in a simple, straightforward style for boys and girls, this book, which is the fourth volume in the "America at Work" series, briefly recounts the growth and development of the rubber industry, and highlights the steps and processes which are used to transform the jungle product into finished manufactured articles. Attention is given to the source of rubber; collecting latex on a typical plantation; preparing crude rubber for market; rubber substitutes; rubber manufacture, particularly the making of footwear and tires; and manufacturing articles from latex. [From the *India Rubber World*.]

THE FORD RUBBER PLANTATIONS. Ford Motor Co., Dearborn, Mich. 8 x 5 in. 36 pp.

This booklet tells the story, in picture form, of the development of the Ford plantations in Brazil. The pictures, taken before and after, as well as the brief text, give an excellent idea of the problems involved in the vast project, as well as the methods by which they are being brought to a successful conclusion. [From *The Rubber Age* of New York.]

RUBBER'S GOODYEAR: THE STORY OF A MAN'S PERSEVERANCE. Adolph C. Regli. Published by Julian Messner, Inc., 8 W. 40th St., New York, N. Y. 1941. Cloth, 6½ by 9½ inches, 248 pages. Price \$2.50.

The story of the perseverance of Charles Goodyear is graphically told here in a straightforward manner, effectively describing the series of misfortunes and triumphs which marked the inventor's life. Written in fictional form, the narrative reads smoothly, dealing with events in chronological order. Goodyear's attempts and ultimate triumph at vulcanizing, his commercial ventures, and Daniel Webster's spirited court defense of Goodyear in the celebrated Goodyear vs. Day case are fully related.

The three concluding chapters, "Pioneers in Rubber", "The Industry in America", and "New Uses for Rubber", describe briefly the sources of rubber, the history of the development of the rubber industry, the stature and attainments of the industry, and the uses and applications of rubber. [From the *India Rubber World*.]

HARD RUBBER MANUAL. Jos. Stokes Rubber Co., Trenton, N. J. 3¼ x 8½ in. 32 pp.

The characteristics and manufacturing procedures for hard rubber are outlined in this new manual, believed to be the first of its kind published. What hard rubber is, how it is compounded and moulded, the creation of moulds, color in the finished piece, factors in design, different forms possible, cost variations and technical terms are among the subjects discussed. Comparisons of physical qualities with those of other modern thermosetting plastics are given. The entire manual is written in clear, concise English, and the text is well presented. [From *The Rubber Age* of New York.]

HIGH POLYMERIC REACTIONS—THEIR THEORY AND PRACTICE. H. Mark and R. Raff. Published by Interscience Publishers, Inc., New York, N. Y. 1941. Cloth, 6½ by 9¼ inches, 476 pages. Author and subject indexes. Price \$6.50.

This, the third volume in this series, continues and expands the scope of the systematic survey of the high polymers, which was begun in the first two volumes of this series—"Collected Papers of W. H. Carothers on High Polymeric Substances", which covered the classical work of one of the foremost early investigators in this field, and "Physical Chemistry of High Polymeric Systems", a book devoted to showing how the fundamental laws of physical chemistry can be applied to the study of high polymers. In the present volume, the aim is to show to what extent physico-chemical measurements offer a quantitative explanation of the mechanisms of polymerization and polycondensations in the light of our present knowledge. Thus, the authors are concerned with an elucidation of high polymer kinetics, developing their theory on the basis of the preparative chemistry of high polymers and the kinetics of organic chemical reactions.

The book is divided into two parts, the first treating the theory and mathematics involved, and the second, covering 145 organic and nine inorganic specific polymerizations, and a section on polycondensations. The four main sections of the first part, with some of the more important subdivisions indicated in parentheses, follow: The Structure of High Polymers (covalent linkage; chain, net, and space polymers; and a list of important polymerizable and condensable substances); Some Data on Experimental Methods (physical and chemical tests; molecular weight and distribution curve; preparation of high polymers and measurement of reaction rates); Fundamentals of Reaction Kinetics (mechanism; fundamental types of reaction; and activation and energy transfer); and General Theory of the Mechanism of Polyreactions (step reactions and chain reactions). Polymerizations treated in the second part of the book which are of direct interest to the rubber chemist include: butene, butadiene and its homologs, isoprene, styrene, chloroprene, and vinyl halogenides and other vinyl compounds. [From the *India Rubber World*.]

PLASTIC MOULDING. By D. A. Dearle. Published by Chemical Publishing Co., Inc., 236 King St., Brooklyn, N. Y. 5½ x 8½ in. 130 pp. \$4.00.

This book is devoted solely to the practical aspects of manufacturing plastic products. In layman English, the author discusses the history of plastics, various materials available, moulding technique, finishing operations, presses, accessory equipment and plant layout, estimates and costs, engineering and design and production management. Completing the "course", as the author terms it, he discusses merchandizing plans for finished products, and offers suggestions for making quotations on competitive work. Review questions appear at the end of each chapter. A subject index is included. [From *The Rubber Age* of New York.]

STANDARDS ON TEXTILE MATERIALS. Published by the American Society for Testing Materials, 260 So. Broad St., Philadelphia, Penna. 6 x 9 in. 387 pp. \$2.00.

In addition to all of the 68 specifications, tolerances, tests and definitions pertaining to textile materials, this publication gives a great deal of other pertinent information, including extended abstracts of four technical papers covering synthetic textile fibers, merit of three rayon taffetas in consumer service, testing breaking strength of fabrics by the pendulum and inclined plane machine, and a correlation between laboratory abrasion tests and service life of men's and women's outerwear. Appendices include extensive photomicrographs of common textile fibers, yarn number conversion tables, psychrometric

table for relative humidity, and a glossary of terms relating to textile materials. Fire proposed standards are published for information. [From *The Rubber Age* of New York.]

MOISTURE CHARACTERISTICS OF CARBON BLACK. By Stuart V. Stoddard and Chester P. Baker. Published by Dept. of Chemical Engineering, Northeastern University, 360 Huntington Ave., Boston, Mass. $5\frac{3}{4} \times 8\frac{3}{4}$ in. 16 pp.

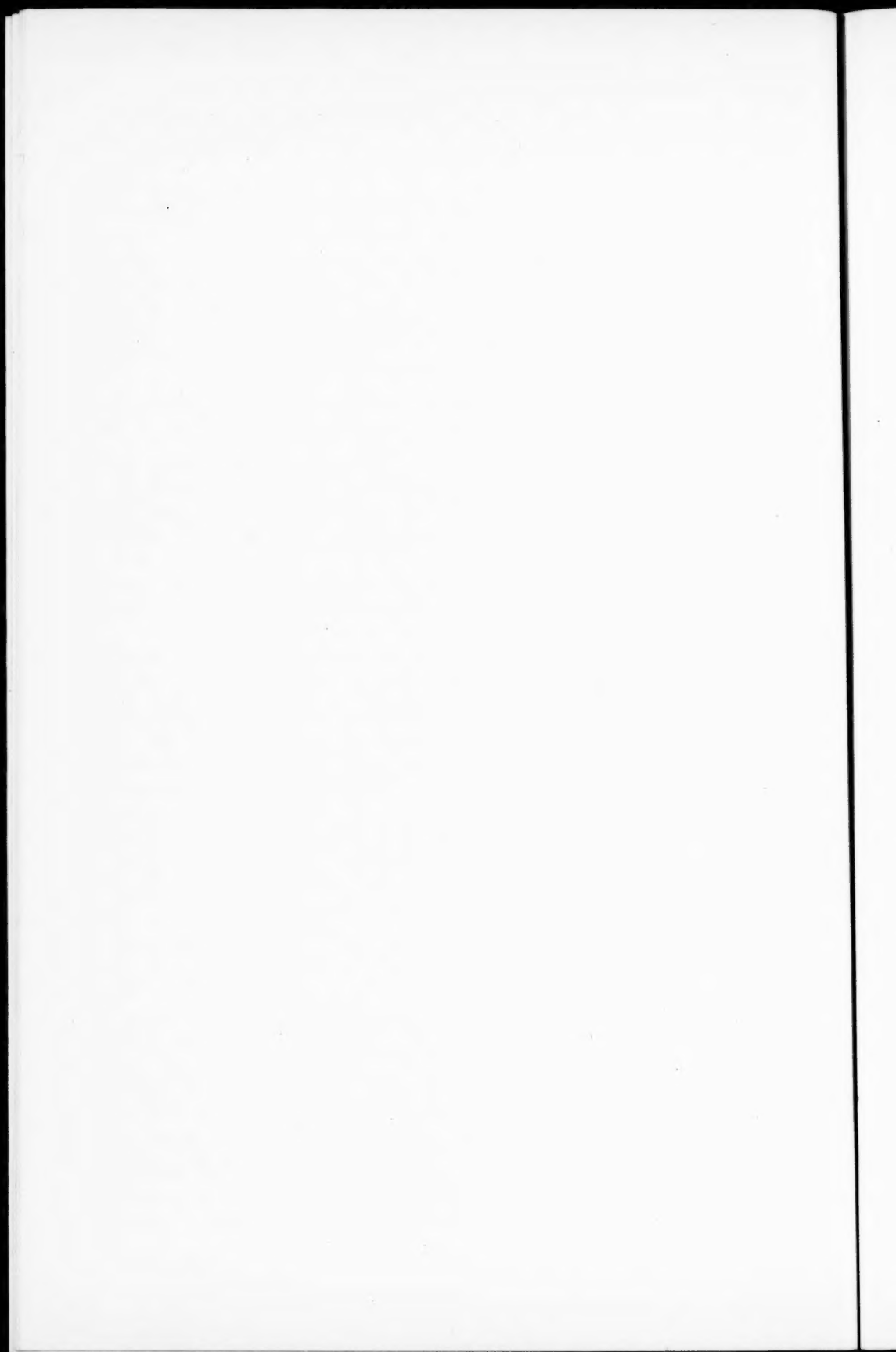
The results of investigations on the amount of moisture present in carbon black throughout the common range of atmospheric humidities, and the rates of sorption and desorption from high to medium and low relative humidities, are given in this booklet. A single grade of pelletized rubber black was used throughout. Equipment used is illustrated, methods of tests are outlined, and conclusions drawn are given. [From *The Rubber Age* of New York.]

THE CHEMICAL FORMULARY. Volume V. Edited by H. Bennett. Published by Chemical Publishing Co., Inc., 234 King St., Brooklyn, N. Y. 1941. Cloth, $5\frac{1}{2}$ by $8\frac{1}{2}$ inches, 676 pages. Indexed. Price \$6.

Following the general arrangement of preceding volumes, the fifth edition contains new and additional formulas, gathered from many sources. A 25-page chapter on "Rubber, Resins, Plastics, Waxes" presents several rubber and latex formulas, together with suggestions on compounding. [From the *India Rubber World*.]

CHEMICAL ENGINEERING CATALOG. Twenty-sixth Annual Edition, 1941. Published by Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. Cloth, $8\frac{1}{4}$ by $11\frac{1}{4}$ inches, 1214 pages. Indexed.

Following the lines of previous editions, the current issue of this standard reference work for the process industries publishes information contributed by several hundred firms manufacturing equipment and supplies for chemical and related industries, including rubber. In addition to cataloging equipment, supplies, industrial chemicals, and raw materials, the book includes sections on: laboratory and reagent chemicals; technical and scientific books; and various charts, tables, and nomographs. [From the *India Rubber World*.]



FRACTIONATION AND MOLECULAR WEIGHT OF RUBBER AND GUTTA-PERCHA *

A. R. KEMP and H. PETERS

BELL TELEPHONE LABORATORIES, INC., NEW YORK, N. Y.

More than ten years ago Whitby²⁰ postulated what is now regarded as an established fact that the soluble portion of crude rubber contains a homologous series of hydrocarbons differing widely in molecular size. We recently showed⁶ that, by the use of a hexane diffusion process, the more soluble portion of crepe rubber can be fractionated into a series of polyprenes with widely different molecular weights. This work has now been extended to show the effect of various solvents and fractionating procedures on both rubber and gutta-percha, using the viscosity method to estimate the average molecular weight of the various fractions. The insoluble portions of crude rubber and latex films have been studied in their relation to the soluble part.

Since crude rubber is soluble to various degrees, depending on its preparation, the solvent, and conditions used in the experiment, it is confusing to speak of sol as a definite fraction without defining all of the circumstances under which it is prepared. The same applies to gel, which should be reserved to describe any rubber in a highly swollen, aggregated state. In the past the portion of rubber soluble in petroleum or ethyl ether has been designated "sol" and the residue "gel". Since this so-called gel rubber contains a large proportion of hydrocarbon soluble in other solvents, such as benzene or chloroform, some new basis of separation is needed.

Much uncertainty has surrounded the phenomena of swelling and solution of rubber in organic solvents. Swelling in solvents occurs in high polymeric rubber, since the diffusion of the large molecules into the solvent is very slow, and until large quantities of solvent enter the rubber, the molecules continue to be held together in the gel by intermolecular forces exceeding those between the solvent and the rubber. The authors take the view that a molecular dispersion of rubber hydrocarbon is best obtained when the rubber is undisturbed and is allowed to enter the solvent phase from the gel by diffusion. On the other hand, if the solution is shaken, gel particles are dispersed and a true solution is not obtained. Solubility or diffusibility in a given solvent decreases with increasing molecular weight, whereas swelling increases as the molecular weight rises. True solutions are therefore more difficult to prepare in the case of higher molecular weight polyprenes.

The extent of solution depends on other factors, such as temperature, time, exposure to light, proportion of rubber to solvent, and surface of rubber exposed. To illustrate the effect of rubber-solvent ratio, various weights of crepe were placed in separate 100-cc. portions of chloroform and hexane for 3 days at 25° C in the dark. In the case of hexane, an additional series was run for 2 hours. The samples in chloroform were placed in weighted bolting-cloth bags

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 33, No. 11, pages 1391-1398, November 1, 1941. This paper was presented before the Division of Rubber Chemistry at the 101st Meeting of the American Chemical Society, St. Louis, Mo., April 10-11, 1941.

to keep the rubber immersed in the solvent. At the end of the immersion periods the viscosity and amount of rubber in the solutions were determined. The results are shown in Figure 1, which illustrates that fractionation, with respect to molecular sizes in solution, does not result from changing the proportion of rubber to solvent within the limits studied. The decreased rate of solution in chloroform resulting from an increase in the proportion of rubber to solvent is believed to be caused by the gel becoming massed in the sack and thus increasing the distance the sol rubber must diffuse to get into solution. In the case of hexane the gel remains firm, and the amount of rubber surface exposed to the solvent is closely proportional to the weight of rubber taken. The solution of rubber is like any other substance. Only by using a poor solvent such as hexane, and by shortening the time, can the smaller molecules be preferentially

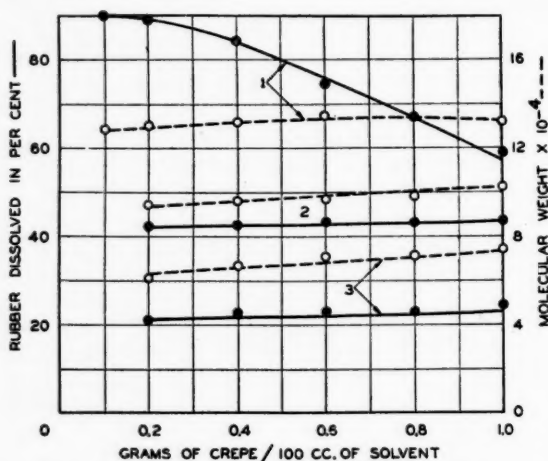


FIG. 1.—Effect of rubber-solvent ratio on solubility and molecular weight of crepe in hexane and chloroform at 25° C.

1. Rubber in chloroform for 3 days.
2. Rubber in hexane for 3 days.
3. Rubber in hexane for 2 hours.

dissolved and a measure of fractionation accomplished, as was previously shown⁶. When 0.1 or 0.2 gram of crepe was placed into 100 cc. of hexane for 9 days, an equilibrium was established, and about 52 per cent of the crepe had entered into solution by diffusion. When 1.5 grams of this crepe was placed in 100 cc. of hexane, longer periods and changes of solvent were required to extract 52 per cent of the rubber, as was found previously⁶. This illustrates that limited solubility becomes a factor when the ratio of rubber to solvent is sufficiently high.

SOLUBILITY AND MOLECULAR WEIGHT OF CRUDE RUBBER

Several years ago the viscosity of a one-per cent solution of crude rubber in benzene was taken as an indication of quality. As early as 1905 Axelrod¹ stated that the higher quality crude rubbers gave more viscous solutions, and a few years later Schidrowitz and Goldsbrough¹³ suggested the viscosity method for evaluating crude rubber. Extensive studies followed these suggestions centering around the measurement of the viscosity of a dispersion made by shaking 1 gram

of crude rubber in 100 cc. of benzene. The results, however, were erratic, and little could be read from them. It is now clear that the rubber in many cases did not completely dissolve, and no consideration was given to the undissolved or dispersed gel portion. Other contributing variables were the effect of dryness of the rubber and the method of preparation of the solution.

To determine the average molecular weight of a larger fraction of crude rubber and latex film than is possible using hexane, an amount of finely cut ribbons of rubber corresponding to 0.01-0.02 base molal solutions (0.068-0.136 gram) was placed in 100 cc. of various solvents in the dark. The solutions were placed in bolting-cloth bags to prevent the gel from dispersing in the solvent. In the case of the heavy solvents, the bags were weighted to keep them immersed. Except where noted, samples were taken from the same piece of R. C. M. A. (Rubber Culture Maatschappij Amsterdam) crepe previously studied^{5, 6} or smoked sheet, to avoid differences due to sample variations. The amount of rubber in solution was determined by drying 25 cc. of the solution in a steam chamber and finally under high vacuum to constant weight. The results given in Table I show that 3 days is sufficient time to allow for solution to take place. Slight oxidation is indicated by lower molecular weight values when the air is not displaced by nitrogen. Agitating the solution every day did not add appreciably to the solvent effect.

The unusual high viscosity of the cyclohexane solution should be noted, since Staudinger and Mojen¹⁸ obtained similar results with this solvent. Cyclohexane was classified by Staudinger as a "good" solvent for rubber, since it required more alcohol or acetone to precipitate rubber from solution than was required, for example, in the case of benzene. Since the present results show that rubber is less soluble in cyclohexane than in benzene, we should classify cyclohexane as inferior to benzene as a rubber solvent.

The method of evaluating crude rubber recommended after these studies is to pipet 100 cc. of the solvent into a bottle in which the finely cut rubber sample corresponding to 0.015 base-molal is placed inside a tight bolting-cloth bag. Air is displaced over the solvent with pure nitrogen, and the bottle placed in a dark cabinet at 25° C for 3 days. The solution is whirled gently for 1 minute before use to mix the contents.

De Vries¹⁹ and later Messenger⁸ found that drying rubber decreased its solubility in benzene. Fol³ recommended drying the crude rubber to constant weight before placing it in benzene. Since crude rubber may vary considerably in moisture content, a study was made of the effect of drying on solubility in benzene and chloroform. These results are given in Table I; they show that the solubility of crude rubber in benzene is greatly affected by drying, but that the effect is relatively small in the case of chloroform. It is evident from these results that chloroform is the preferred solvent, since the effect of dryness of the rubber is not an important factor affecting solubility. Chloroform is also readily evaporated at low temperatures, which makes the estimation of concentration more reliable. Merck's reagent-chloroform was used in this investigation, and is the grade recommended. This product contains about 0.7 per cent of alcohol. Although this quantity of alcohol reduces the viscosity of an alcohol-free chloroform solution of crepe rubber by about 10 per cent, its presence aids solution, and is desirable to obtain greater chemical stability.

The results in Table I illustrate the value of such a standard procedure for judging the molecular state of crude rubber and latex films. A nervy crude rubber such as Bolivian fine para has a high average molecular weight and a high

TABLE I
 VISCOSITY-MOLECULAR WEIGHT OF SOLS FROM CRUDE RUBBER

Rubber	Base molarity of sample	Solvent	Sol concn., base molarity	% Sol rubber	η_r	$M = (\log \eta_r / C) \times 0.75 \times 10^4$
No. 1 smoked sheet.	0.0200 ^d	Chloroform ^g	0.0167	83.5	1.990	134,000
	0.0200 ^e	Chloroform ^g	0.0171	85.5	1.960	128,000
	0.0200 ^f	Chloroform ^g	0.0173	86.5	1.955	126,000
	0.0200	CCl ₄ ^g	0.0158	79.0	2.000	143,000
	0.0200	Benzene ^g	0.0163	81.5	2.050	143,000
	0.0200	Cyclohexane ^g	0.0135	67.7	1.921	157,000
R. C. M. A. crepe...	0.0150	Chlorobenzene ^h	0.0125	83.5	1.731	142,000
	0.0200	Chloroform ^h	0.0169	84.5	1.958	129,000
	0.0150	Chloroform ^h	0.0129	86.0	1.703	134,000
	0.0100	Chloroform ^h	0.00882	88.2	1.438	138,000
	0.0200	Benzene ^h	0.0150	75.0	1.917	141,000
	0.0150	Benzene ^h	0.0112	74.7	1.632	142,000
	0.0100	Benzene ^h	0.00754	75.4	1.410	147,000
No. 1A smoked sheet	0.0150	Benzene ⁱ	0.0113	75.7	1.617	139,000
	0.0150	Benzene ^j	0.00835	55.6	1.406	133,000
	0.0150	Benzene ^k	0.00671	44.7	1.249	108,000
	0.0150	Benzene ^{g, k, l}	0.00671	44.7	1.261	113,000
	0.0150	Benzene ^{h, k, m}	0.00524	34.9	1.138	80,000
Bolivian fine para...	0.0150	Benzene	0.00765	51.0	1.464	162,000
	0.0150	Benzene ^j	0.00371	24.7	1.156	128,000
1A smoked sheet....	0.0150	Chloroform	0.0128	85.0	1.675	132,000
	0.0150	Chloroform	0.0129	86.0	1.675	131,000
	0.0150	Chloroform ^k	0.0123	82.0	1.640	131,000
Bolivian fine para...	0.0150	Chloroform	0.00924	61.6	1.613	168,000
	0.0150 ^f	Chloroform	0.00924	61.6	1.613	168,000
	0.0150	Chloroform ^j	0.00906	60.4	1.555	158,000
Up-river fine para, mill-washed and air-dried	0.0169	Chloroform	0.01124	66.4	1.663	147,000
Java purified crepe.	0.0150	Chloroform	0.0150	100.0	1.625	106,000
Latex film ^a	0.0166	Chloroform	0.01035	62.3	1.610	150,000
Latex film ^a	0.0171	Hexane	0.00106	6.4	1.010	30,000
Latex film ^b	0.0157	Hexane	0.00153	9.7	1.033	69,000
Latex film ^b	0.0163	Chloroform	0.01088	66.6	1.820	179,000
Latex coagulum ^c ...	0.0159	Hexane	0.000882	5.6	1.010	36,000
Latex coagulum ^c ...	0.0160	Chloroform	0.009117	56.8	1.625	173,000

^a Ammonia-preserved, dried on glass plate over P₂O₅ in dark in a vacuum.

^b Ammonia-preserved, dried on glass plate in air in darkness; washed in water and redried over P₂O₅ in a vacuum in darkness.

^c Ammonia-preserved latex coagulated with acetic acid, pressed free of occluded water, and dried in a vacuum in darkness over P₂O₅.

^d 1 day in solvent.

^e 3 days in solvent.

^f 6 days in solvent.

^g Air over solution in dark and undisturbed.

^h Nitrogen over solution in dark and undisturbed.

ⁱ Standard procedure.

^j Rubber vacuum-dried 18 hours over P₂O₅.

^k Rubber vacuum-dried 13 days over P₂O₅.

^l Benzene saturated with water.

^m Benzene specially dried.

residual gel content, whereas a soft, weak rubber such as Java purified crepe has a low average molecular weight and a low content of difficulty soluble gel.

Various investigators have given the average molecular weight of crude rubber as ranging from 120,000 to 180,000, using the Staudinger viscosity method. The values are changed to 90,000 and 135,000, respectively, when using the recently determined⁷ K_{cm} value of 0.75×10^4 . The present results in Table I are higher, since the insoluble portion was excluded from the determination.

NATURE OF INSOLUBLE RESIDUE

Gel rubber, defined as that portion of crude rubber insoluble in ether or petroleum ether, still contains about 30 per cent rubber hydrocarbon which can be dissolved in chloroform. The present study shows that there is a sharp separation between the chloroform-soluble portion and the residue which remains quite insoluble after long periods of standing in this solvent in the absence of oxygen. This chloroform-insoluble gel constitutes between 10 and 15 per cent of ordinary crepe or smoked sheet, and contains the bulk of the proteins and ash. In one sample an ash content of 1.32 per cent and a protein content of 13.5 per cent was found, the remainder being rubber hydrocarbon.

The insoluble residue on drying is light brown and non-tacky, and shows excellent elasticity, high modulus, and an ultimate elongation of 120 per cent. (The x-ray diffraction patterns of this and other rubber fractions were kindly furnished by C. S. Fuller of these laboratories, under whose direction the x-ray work was carried out.)

Figure 2A demonstrates that highly oriented fiber patterns can be obtained from a high-molecular, sol rubber fraction, since sufficient interaction occurs between the molecules to bring about crystal formation on stretching. This has already been pointed out by Gehman⁴. When low-molecular sol rubber is stretched, this interaction is lacking and the amount of elongation is obviously without significance.

In the case of the so-called gel rubbers, *i.e.*, the residues left after exhaustive solvent extraction, differences are observed, depending on the thoroughness with which the soluble portions are removed and the nature of the residue. Thus, stretching of crepe rubber, from which 52 per cent sol had been extracted by petroleum ether at room temperature, produced a high degree of orientation (Figure 2B), comparable with that observed in Figure 2A. On the other hand, the insoluble gel rubber remaining after chloroform extraction of 86 per cent of crepe (Figure 2C) is not capable of being so completely oriented. A possible explanation is that the extraction has so concentrated the cross-linked part of the rubber that the crystalline portions which form as a result of stretching are prevented from attaining perfect alignment.

Figures 2D and E were made from samples of chloroform-extracted latex film and Bolivian fine para from which a maximum of 62 per cent sol had been removed. The latex film rubber apparently contains a chloroform-insoluble, high-molecular hydrocarbon which is highly distensible and easily oriented. The presence of any cross-linked portion is masked, perhaps because of the presence of the large proportion of the highly orienting portion in which the cross-linked fraction may be dispersed. The chloroform-extracted residue from Bolivian fine para gives an x-ray diagram which indicates the presence of more cross-linking than exists in the chloroform residue from latex film. It is possible that this may have resulted from the smoking operation performed in the preparation of this rubber from

latex. This type of rubber is definitely stronger and has better elastic recovery than smoked sheets; however, this may be due in part to the fact that smoked sheets have been rolled during preparation, which causes some breakdown.

To obtain further evidence on the nature of this chloroform-insoluble portion of natural rubber, small samples were passed repeatedly through tight rolls, and their solubilities in chloroform and the viscosities of the solutions were determined. These results are presented in Table II, in comparison with some milled and unmilled synthetic rubbers. The limited solubility in relation to the low

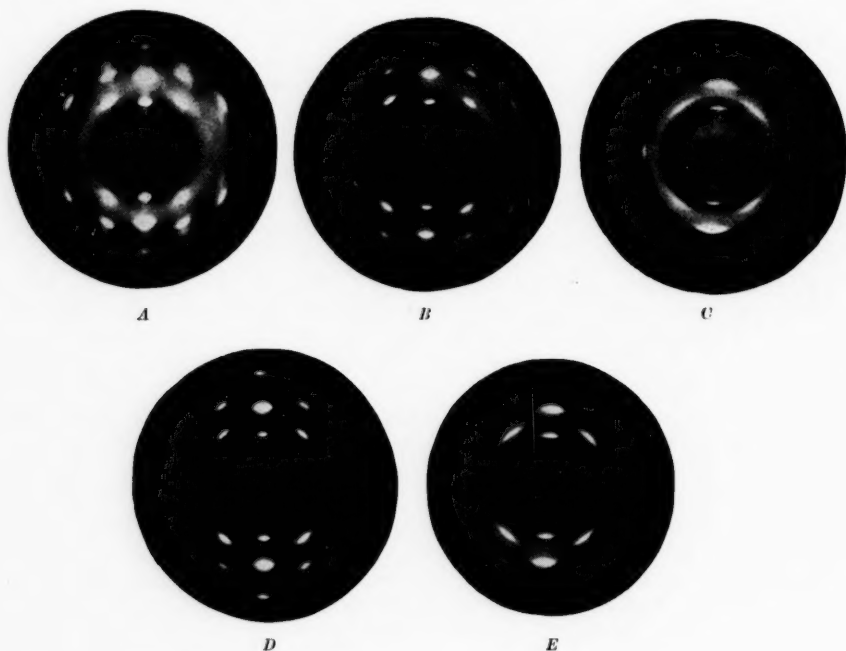


FIG. 2.—X-ray photographs of rubber fractions under maximum stretch.

- A. High-molecular chloroform sol from crepe, 800 per cent elongation.
- B. Residue from petroleum ether extraction of crepe, 500 per cent elongation.
- C. Residue from chloroform extraction of crepe, 120 per cent elongation.
- D. Residue from chloroform extraction of latex film, 700 per cent elongation.
- E. Residue from chloroform extraction of Brazilian fine para, 180 per cent elongation.

viscosity-molecular weight value of the chloroform-insoluble portion of crepe after milling is evidence that this substance is not strictly a linear polymer, but is possibly a three-dimensional type. Therefore the average molecular weights calculated by the viscosity method will be lower, since three-dimensional or branched-chain polymers contribute less to the viscosity than linear ones. The mechanical breakdown of such three-dimensional gel structures apparently results in organized groups of cross-linked chain polymers being broken into small fragments. The sols from this milled material remained elastic and nontacky, and their elongation was not very different from that of the unmilled material. In this respect they behaved like some of the synthetic rubbers. The iodine value of the rubber sol derived by milling the insoluble fraction does not indicate extensive cross-linking through mutual saturation of the double bonds. A type

of oxygen cross linking may be involved. The low nitrogen content also indicates that the protein can be separated from the chloroform-insoluble type of hydrocarbon by milling and subsequent extraction.

The milling experiments indicate that the ammonia-preserved latex as well as the Bolivian fine para contain high-molecular-weight hydrocarbon similar to the sol in structure.

FRACTIONATION OF RUBBER

Much of Staudinger's work on the viscosity-molecular weight of rubber was carried out on rubber purified by the Pummerer and Pahl alkali process¹², using latex. Although this and similar methods are effective in removing "resin" and

TABLE II
VISCOSITY OF MILLED GEL FROM CREPE IN CHLOROFORM COMPARED WITH
SYNTHETIC RUBBER

No. of times through tight mill rolls	Substance taken (gram)	Days in 100 cc. of CHCl ₃	% Sol rubber	Base molarity of sol	η_r	$M = (\log \eta_r / C) \times 0.75 \times 10^4$
14% INSOL. RESIDUE FROM CHLOROFORM EXTN. OF CREPE ^a						
8	0.1055	3	23.5	0.00365	1.025	22,500
25 ^b	0.175	2	60.5	0.0155	1.140	27,500
40% INSOL. RESIDUE FROM CHLOROFORM EXTN. OF WASHED LATEX FILM						
5	0.1560	4	61.5	0.0141	1.503	94,000
10	0.1630	4	70.4	0.0170	1.490	77,000
40% INSOL. RESIDUE FROM CHLOROFORM EXTN. OF BOLIVIAN FINE PARA						
5	0.1580	6	27.3	0.00635	1.175	82,000
10	0.1720	6	40.9	0.01035	1.250	70,000
BUNA 85 (BUTADIENE SODIUM POLYMER)						
.....	0.54	12	62.9	0.0796	1.808	24,200
5 min.	0.270	6	100	0.0500	1.625	31,500
NEOPRENE-GN						
.....	0.8852	12	36.3	0.0428	1.363	23,600
5 min.	0.4425	6	97.6	0.4881	1.545	29,000

^a Per cent analysis of insoluble gel: nitrogen, 2.25; ash, 1.32.

^b Analysis of rubber sol: iodine value, 355; carbon, 86.97%; hydrogen, 11.70%; nitrogen, 0.21%.

nitrogenous components, they make the rubber hydrocarbon extremely susceptible to oxidation and depolymerization by removal of the natural antioxidant. Staudinger¹⁵ separated this rubber into what he termed "sol" or easily soluble portion having a molecular weight of 38,000 and a difficultly soluble portion with a molecular weight of 105,000, using a K_{cm} value⁷ of 0.75×10^4 . The present, as well as a previous study⁶, shows that rubber with these average molecular weights is readily soluble in a variety of solvents and is in a lower average molecular state than most of the hydrocarbon present in high-quality plantation rubber or ammonia-preserved latex (Table I).

Staudinger and Bondy¹⁶ employed benzene in separating 50 per cent of a "freely soluble" fraction from crude rubber and 18 per cent of a "difficultly soluble" fraction; the latter had an average molecular weight of 139,000 using a K_{cm} value⁷ of 0.75×10^4 , which accords well with our findings.

Since small differences in the molecular weight of polymers result in small variations in their solubility, there is little hope of developing a fractionating scheme to yield products in which the molecules are of identical size. Special techniques must be employed to fractionate polymer mixtures of widely varying molecular weights into a series of products having even moderately narrow ranges of molecular sizes. A product ranging 25 per cent on each side of the average should be considered a fairly narrow fraction. In the present investigation crepe rubber was separated into soluble polyprene fractions ranging in average molecular weight from about 9000 to 187,000, using a K_{cm} value⁷ of 0.75×10^4 . Each of these fractions, however, covers a polymeric range which would require repeated fractionation to narrow. It is doubtful if such additional fractionation would add much information to that already obtained.

Diffusion method.—In a previous investigation⁶ the soluble portion of acetone-extracted crepe was fractionated by diffusion in hexane into twelve fractions. The average molecular weight of succeeding fractions showed an increase from 67,000 to 178,000, using a new K_{cm} value⁷ of 0.85×10^4 for hexane. If each of these separate fractions was refractionated by the same process, further separations could be made. For example, it is now known that the more soluble fraction contains rubber polymers having much lower average molecular weights. The rate of diffusion decreases with increase in polymeric size, but these differences are not sufficiently sharp to separate different sizes by the diffusion method alone.

The authors' experience shows that "good" solvents, such as benzene or chloroform, are not so satisfactory in a diffusion process as are poorer solvents, such as hexane or ether, in which rubber hydrocarbon is less soluble. In this connection Bloomfield and Farmer² recently employed a "poor solvent" mixture of equal volumes of petroleum ether and acetone and separated small amounts of low-polymer rubber containing oxygen. A rubber fraction constituting 15 per cent of the whole was dissolved by increasing the petroleum ether-acetone ratio to 60-40, but when this ratio was increased to 62.5-37.5, a fraction amounting to 70.0 per cent of the original rubber quickly dispersed. The latter mixture is a good solvent for rubber, and this accounts for its failure to fractionate closely. On the other hand, Bloomfield and Farmer's results² show that mixtures high in acetone, with limited solvation power, are excellent for use in separating the lower molecular weight fractions of rubber by diffusion. The ideal conditions for fractionation by diffusion would be to employ a series of solvents of broad solvent action, each succeeding one having slightly increased solvent power. This, however, is difficult to realize.

To study Bloomfield and Farmer's method, 200 grams of R. C. M. A. crepe was treated with 1500 cc. of a mixture of 50-50 acetone-hexane at room temperature in the dark. The air was displaced over the solution with lamp nitrogen. After various periods allowed for solvation, this treatment was repeated with 1000-cc. portions of fresh solvent. After evaporation of the solvent, each fraction was extracted with warm acetone to remove resins, and the hexane ratio was increased gradually. The iodine value and the viscosity-molecular weight of the acetone-insoluble portions of the early fractions were then determined. The results, presented in Table III, not only confirm the findings of Bloomfield and Farmer, but also indicate that crepe rubber contains fractions having molecular weights ranging between 9000 and 30,000. A similar study was made, using washed and dried ammonia-preserved latex films; the results (Table III) also show the presence of low polymers in this type of rubber.

The extent to which the solvent power of hexane towards rubber is affected by the addition of polar solvents is shown in Figure 3. These experiments involved placing 0.2-gram samples of air-dried latex film in 100 cc. of hexane to which were added various proportions of acetone and different alcohols. After 3 days in the constant-temperature room in the dark at 25° C, the rubber which had entered into solution was determined. The curves in Figure 3 show the effect of polar solvents on the solubility and on the precipitability of rubber in hexane. It appears that the alcohol with the highest dielectric constant increases solvation most, and extends this effect over the narrowest range of

TABLE III
EXTRACTION WITH HEXANE-ACETONE MIXTURES

Fraction No.	Extn. period (hrs.)	Extract, %		Mol. wt. of rubber ^a	Iodine value of rubber	Remarks
		Resin	Rubber			
EXTRACTION OF CREPE						
1	24	1.23	0.19	9,000	359	Soft, pasty
2	24	0.61	0.23	10,400	361	Soft, pasty
3	72	0.31	0.38	12,700	363	Firmer, rubber-like
4	72	0.16	0.35	13,500	363	Like heavily milled rubber
5	96	0.13	0.29	13,900	—	Same
6	168	0.07	0.28	16,000	—	Same
7	72	0.03	0.27	20,800	—	52-48 hexane-acetone
8	96	0.08	0.35	30,300	—	54-46 hexane-acetone ^b
Total.....		2.62	2.34			
EXTRACTION OF WASHED LATEX FILM ^c						
1A	24	1.64	0.22	9,700	—	Soft, pasty
2A	72	0.38	0.23	12,300	—	Firm, rubber-like
3A	96	0.12	0.22	15,100	—	Same
4A	96	0.06	0.35	20,600	—	52-48 hexane-acetone
5A	72	0.03	0.63	30,600	—	54-46 hexane-acetone ^b
6A	96	—	0.67	32,400	—	54-46 hexane-acetone
7A	144	—	0.92	81,000	—	56-44 hexane-acetone
8A	72	—	1.25	92,200	—	Same
Total.....		2.23	4.49			

^a Using K_{em} of 0.75×10^4 .

^b Large increase in swelling noted.

^c Ammonia-preserved latex, dried in darkness on a glass plate in air at room temperature, washed free from water-solubles in distilled water, and redried under same conditions.

composition. Acetone functions somewhat differently from the alcohols, but basically its polar nature results in similar solvation effects. In Figure 4 the effect of adding glacial acetic acid to the hexane up to 1 per cent by volume is shown. Thus, the addition of a very small amount of acetic acid greatly increases the solvent power of hexane for rubber. It was noted that, on shaking, the insoluble residue was easily dispersed in the cases where acetic acid was added. This indicates a somewhat different mechanism or extent of action than is the case for alcohol addition.

Combined diffusion and precipitation methods.—A study was made of diffusion of crepe rubber into chloroform followed by precipitation with methanol. In one experiment 2.5 grams of finely cut crepe were placed in a weighted bolt-

ing-cloth sack and immersed in 500 cc. of chloroform. The solution protected by nitrogen was decanted after standing in the dark for definite periods at 25° C. The viscosity-molecular weight of this solution was determined and the rubber precipitated with methanol. The unprecipitated portion was separated by careful evaporation of the solvent, using a stream of nitrogen, and its molecular

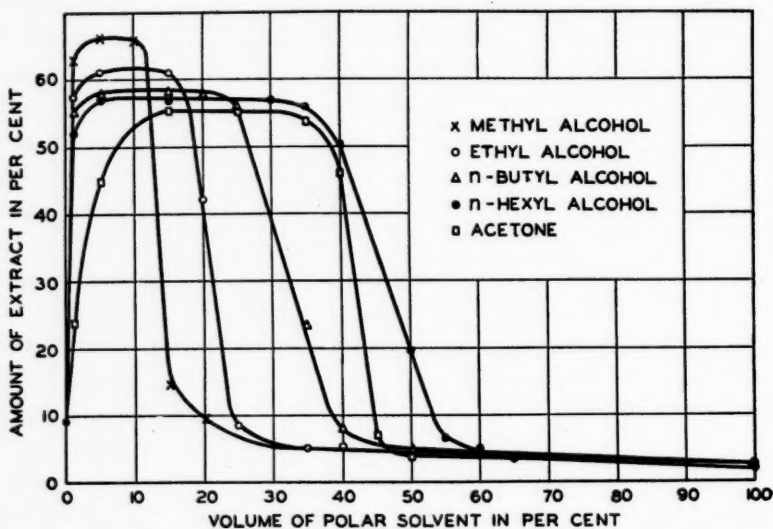


FIG. 3.—Effect of adding polar solvent on solubility of latex film in hexane.

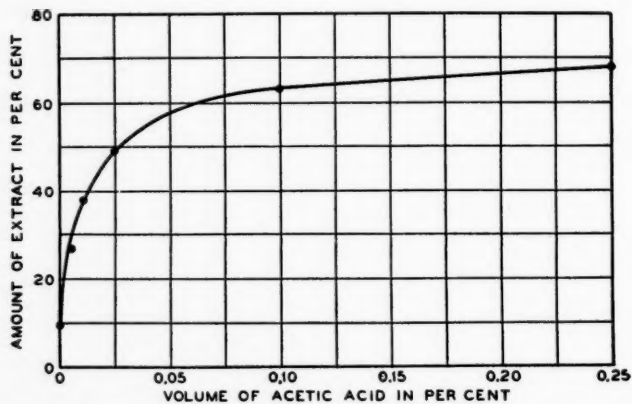


FIG. 4.—Effect of acetic acid on solubility of latex film in hexane.

weight was determined after complete removal of solvent in a stream of nitrogen. The residual crepe was covered with additional 500-cc. portions of chloroform, and the operations were repeated three times. The results, given in Table IV, show that precipitation methods are effective in fractionating crepe rubber from chloroform solution. The weighted average molecular weight of the precipitated and unprecipitated portion of the first chloroform fraction is the same as that

of the rubber in the original chloroform solution; this shows that the procedure avoided a molecular breakdown of the rubber hydrocarbon. Throughout this work the rubber fractions were protected with nitrogen, and were immediately dried and placed in solution for molecular weight estimation, since purified rubber is susceptible to oxidation, even when kept in greatly reduced oxygen concentration in darkness.

The method of solution of crepe or smoked sheet in chloroform by diffusion and decantation from the difficultly soluble swollen gel, followed by precipitation of the rubber from solution by addition of methanol as outlined in the present investigation, furnishes a simple method for preparing a high-molecular fraction of rubber hydrocarbon in good yield. These high-molecular fractions closely resemble well vulcanized, pure-gum rubber in elasticity, strength, and permanent set.

Cooling Procedure.—Midgley, Henne, and Renoll¹¹ fractionated crepe rubber from solution in a 68-32 benzene-alcohol mixture by a cooling procedure. Since

TABLE IV
SOLUTION AND PRECIPITATION OF CREPE RUBBER IN CHLOROFORM ^a

Fraction No.	Days of diffusion	Wt.-% of total rubber in fraction	Mol. wt. in chloroform ^b	Yield of rubber by pptn. (%)	Remarks
I	3	76.5	136,000	—	—
Ia	—	52.8	169,000	69	I pptd. with CH ₃ OH
Ib	—	23.7	51,000	31	Rubber unpptd. from I
Ic	—	48.4	187,000	91	Ia redissolved in CHCl ₃ , repptd.
II	3	7.7	152,000	—	} Soln. too dilute to form ppt. on adding CH ₃ OH
III	4	1.6	—	—	
IV	7	0.1	—	—	
Residue ^c	—	14.1	—	—	100—(I+II+III+IV)

^a 2.5 grams R. C. M. A. crepe in bolting-cloth sack, immersed in 500 cc. CHCl₃.

^b Using K_{cm} of 0.75×10^4 .

^c Solvent replaced by mixture of 85 per cent C₆H₆ and 15 per cent CH₃OH by volume; 1.04 per cent dissolved after standing 3 days.

these authors did not determine the molecular weight of the different fractions, an attempt was made to repeat this work on the R. C. M. A. crepe employed in this and previous studies^{5, 6}. It was found that this crepe did not dissolve completely in the mixed solvent at 50° C and, when cooled to 42°, the viscosity was so high that the gel could not be readily separated from the solution. Midgley and his coworkers employed a crepe with a nitrogen content of only 0.15 per cent, which indicates a purified type, probably lower in average molecular weight and more soluble. In view of the difficulty in the present case, the rubber was further precipitated by cooling the solution to 0° C for 1 hour. It was then easily separated from the solution by simple decantation. The solution was evaporated in a stream of nitrogen, the residual rubber, which was soft and sticky, was extracted with acetone, and its average molecular weight was determined in chloroform. The rubber amounted to 3.97 per cent of the whole, and had an average molecular weight of 18,000; the resin portion amounted to 2.97 per cent on the rubber. In the experiments of Midgley and his co-workers, 16.4 per cent of the original rubber was unaccounted for. Although this portion was not referred to, it was probably the unprecipitated fraction.

In the later investigation, Midgley and Henne¹⁰ worked with an ether-soluble fraction of rubber from spray-dried latex. This rubber was separated into six fractions, and their viscosities in benzene were determined. We calculated the

following molecular weights of these fractions, which constituted about 75 per cent of the original ether-soluble fraction:

Fraction	Per cent	η_r	$M = \frac{\log \eta_r \times 0.75 \times 10^4}{C}$
A ₁	25	1.92	62,000
A ₂	4.2	2.67	94,000
A ₃	6.2	2.67	94,000
A ₄	4.2	2.67	94,000
A ₅	2.1	—	—
BB	33	3.25	113,000

In view of these results, fractionation by cooling does not appear to offer much promise over the procedures already described. Its failure in the case of whole crude rubber was disappointing.

POLYMERIC STATE OF FRESH AND AMMONIA-PRESERVED LATEX

The need for studying the nature of the hydrocarbon in fresh latex from trees of various ages and environment was first pointed out by the authors⁵. Results were recently obtained which show that ammonia-preservation of fresh latex causes the rubber to become less soluble in organic solvents. This indicates that polymerization of fresh latex results from standing in contact with ammonia. We found in May, 1939, that fresh latex film from *Hevea* located on the U. S. Government gardens at Coconut Grove, Florida, yielded large fractions soluble

TABLE V
COMPARATIVE SOLUBILITY OF FRESH AND AMMONIA-PRESERVED LATEX
FILMS IN PETROLEUM ETHER

Type of latex	% Soluble in petroleum ether ^a
Fresh Florida <i>Hevea</i> , May, 1939	
Tree 1527	36.6
Tree 1096	56.6
Mixed, trees 1096 and 1527	45.9
Bulked latex from 46 trees	52.0
Fresh Java latex ^b	
Av. bulked at Tjipetir, Java, Aug., 1940	40.1 ^d
Old tree, ordinary tapping, resin 4.6%	46.2
Ordinary tree, first tapping, resin 4.6%	42.4
Old tree, ordinary tapping, resin 4.6%	45.3 ^e
Costa Rica latex ^c	
0.5% ammonia 5 days after tapping	17.4
0.5% ammonia 2 weeks after tapping	10.1
Regular ammonia-preserved latex, 6 weeks to 3 months old...	5.5-10.0

^a After 72 hours ⁵.

^b Information from H. R. Braak.

^c Supplied by Goodyear Tire and Rubber Company.

^d 48-hour extraction period.

^e 96-hour extraction period.

in hexane. Recently, through the courtesy of H. R. Braak of Batavia, Java, some results obtained in the laboratories of the Netherlands East Indies Government Plantations by A. de Leeuw were sent to us, and lead to the same conclusion. Fresh latex preserved with only 0.5 per cent ammonia was also obtained from the Goodyear estate in Costa Rica through the courtesy of The Goodyear Tire

& Rubber Company. This latex was only 5 days old when a film was made; the soluble portion was determined, and found to be higher than in films of the same latex 2 weeks old or in the regular ammonia-preserved product from the Far East. The results in Table V lead to the conclusion that the rubber in fresh latex is in a different state from that in the ammonia-preserved product. Tests on samples of fresh latex collected over a wider variety of conditions are being carried out in Java under Braak's direction. Since plantation crude rubber has a high sol content, it now appears that the source of this exists in the fresh latex, and that it is augmented by breakdown in the sheeting and creping operations. Before obtaining results on fresh latex, we were of the opinion that estate processing may have accounted for all the sol fraction through oxidation⁵.

The nature of the rubber in ammonia-preserved latex was studied by subjecting films to various treatments before extraction and by employing various solvents. Table I shows that chloroform dissolves over 60 per cent, whereas hexane

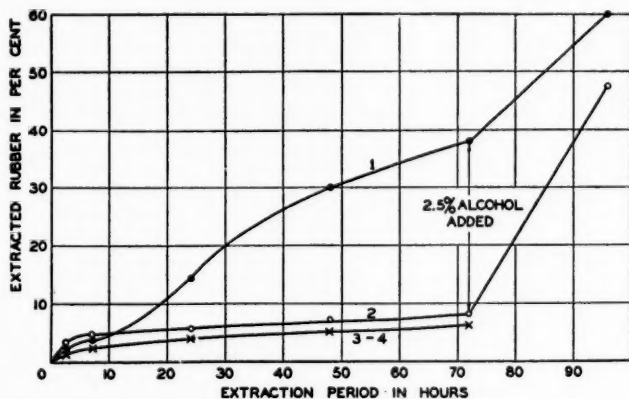


FIG. 5.—Sol rubber from latex film in different solvents.

1. Film dried in air in darkness, placed in benzene.
2. Film dried in air in darkness, washed in distilled water, redried over P_2O_5 in a vacuum in darkness, and placed in hexane.
3. Film dried in air in darkness, placed in hexane.
4. Film dried over P_2O_5 in vacuum in darkness, placed in hexane.

dissolves only 6 per cent of an ammonia-preserved latex film or latex coagulum. If 2.5 per cent alcohol is added to the hexane, over 60 per cent dissolves. This shows that ammonia has produced a type of aggregation which requires a polar solvent to overcome. Another series of tests was made, using the extraction method previously described⁵. The results (Figure 5) show that the latex rubber does not dissolve at first in a nonpolar solvent, such as benzene, but after continued extraction it becomes soluble. The increased rate of solution in benzene after the first extractions may be due to slight oxidation of the rubber; however, it is also possible that moisture or some other polar substance extracted from the latex film may have increased the solubility. In view of the erratic solubility effect of benzene on latex film and crude rubber, the results obtained in the past with this solvent may be questionable.

FRACTIONATION OF BALATA AND GUTTA-PERCHA

Staudinger¹⁷ separated balata hydrocarbon from balata latex, and fractionated it from solution by a cooling procedure. Solutions of 0.5 base-mole concentration

of these fractions were prepared and their viscosities determined. The first fractions had higher viscosities than the later ones; however, all solutions had high relative viscosities, and the molecular weight values were not calculated. The conclusion was reached that the balata contains hydrocarbon fractions varying considerably in molecular size.

In view of Staudinger's results, it seemed desirable to determine the approximate molecular weight distribution of balata and gutta-percha hydrocarbon, especially since no previous fractionating study of gutta-percha has been re-

TABLE VI
FRACTIONATION OF BALATA HYDROCARBON FROM LATEX BY DIFFUSION INTO
BENZENE^a AT ROOM TEMPERATURE IN DARK

Fraction	Concn., base molarity ^b	η_r	$M = (\log \eta_r / C) \times 0.75 \times 10^4$
1st ext., 36.7% in 6 days.....	0.0360	1.542	39,000
2nd ext., 29.3% in 11 days.....	0.0344	1.562	42,300
3rd ext., 8.5% in 4 days.....	0.0500	1.785	37,700
Residue dissolved in hot C ₆ H ₆ , filtered.....	0.0158	1.236	43,600
Whole extd. balata dissolved in hot C ₆ H ₆ , filtered..	0.0408	1.673	41,000 ^c

^a Balata latex spread on glass plate and dried over P₂O₅ in darkness; extracted repeatedly with cold hexane to remove resin, followed with distilled water to remove serum solids; dried over P₂O₅; 4.009 grams placed in 100 cc. benzene.

^b Determined by weighing the residue from 20 cc. of solution; solution diluted to obtain relative viscosities in the range 1.5-1.8 where possible.

^c Staudinger¹⁷ reported 51,000 for average molecular weight of balata hydrocarbon prepared from latex, which becomes 35,700 when K_{cm} of 0.75×10^4 is used.

TABLE VII
EFFECT OF PRECIPITATION ON VISCOSITY-MOLECULAR WEIGHT OF GUTTA-PERCHA
HYDROCARBON FROM LEAVES^a

Gutta-Percha	Concn., base molarity	η_r	$M = (\log \eta_r / C) \times 0.75 \times 10^4$
Whole, in chloroform.....	0.0250	1.455	48,800
	0.0333	1.633	48,000
	0.0500	2.050	46,700
Pptd. from chloroform by CH ₃ OH, 83.7% yield (chloroform soln.)	0.0437	2.008	51,300 ^b
Whole, in benzene.....	0.0235	1.368	43,500
	0.0313	1.510	42,800
	0.0470	1.822	41,300
	0.0940	3.059	38,800

^a White Tjipetir estate gutta.

^b This value would be 69,200, using K_{cm} of 10^4 .

ported. Balata hydrocarbon from latex and gutta-percha hydrocarbon from leaves have been fractionated in benzene by diffusion and precipitation. The results in Table VI and VII show the exceptional uniformity and narrow distribution range of gutta hydrocarbon from balata as well as from leaf gutta-percha. The molecular weight values for balata hydrocarbon in benzene are in good close agreement with that found by Staudinger and Bondy¹⁷.

The chemical properties of rubber and gutta-percha are identical, and the differences in their x-ray crystal patterns have been accounted for by assuming they are stereoisomers. Meyer and Mark⁹ favor the *cis* form for rubber hydrocarbon, because of its lower density and lower melting point and the difference in x-ray patterns of the two hydrocarbons which points towards a *cis* form in rubber. Since the *trans* form is more symmetrical, it would be expected to crystal-

lize more readily than the *cis* modification, which is found to be the case. Staudinger¹⁴, on the other hand, ascribed the *cis* form to gutta hydrocarbon, stating that its crystallizability may depend more on its lower molecular weight than upon symmetry in structure.

Gutta hydrocarbon is insoluble in cold ether or petroleum ether, whereas milled rubber with the same average molecular weight as gutta is freely soluble in these solvents. Gutta has a tensile strength of over 20,000 pounds per square inch after about 400 per cent cold drawing, and shows reversible elasticity only after being cold drawn. In this respect it is like the polyesters and polyamides of Carothers. Rubber of the same average molecular weight has little elasticity or strength, and is much softer than gutta. These differences between gutta and rubber can be partially accounted for by the enhanced forces between the gutta molecules arising from their crystallinity. The higher density crystallinity, hardness, and strength of gutta compared with rubber can be ascribed to a closer molecular packing in gutta than in rubber.

CONCLUSIONS

1. Evaporated latex films and Bolivian fine para contain a chloroform-soluble fraction of about 62 per cent, whereas the soluble portion of crepe and smoked sheets is about 86 per cent. The average molecular weight of these sols, which contain the low polymers and "resin", range from about 130,000 to 180,000, the more soluble type having the lower value.

2. Diffusion and precipitation methods were employed to fractionate R. C. M. A. crepe, and the following data indicate the approximate composition and molecular weight range of the soluble hydrocarbon fractions separated:

Fraction	Mol. wt. range	Content (%)
Resins	—	2.7
Hexane-acetone	9,000-30,000	2.3
Hexane	60,000-160,000 ⁶	50.0
Hexane insol., chloroform sol.	160,000-190,000	31.0
Chloroform-insol. gel + protein and ash..	—	14.0

3. The chloroform-insoluble portion of crepe contains a nonlinear type of hydrocarbon, judged by x-ray and viscosity studies. These methods show that the chloroform-insoluble portion of ammonia-preserved latex films contain extremely high-molecular rubber hydrocarbon which is easily oriented to give the regular x-ray crystalline pattern for rubber.

4. Freshly tapped latex contains a large proportion of petroleum-ether-soluble fraction, which becomes insoluble in this solvent on standing in the presence of ammonia. Ammonia-preserved latex films are soluble in chloroform or in hexane containing alcohol-acetone or acetic acid; this insolubility is thus an association effect, which is overcome by the addition of a polar solvent.

5. Viscosity studies on fractions of balata and gutta-percha show that their hydrocarbons have an average molecular weight of about 42,000 and cover a narrow polymeric range.

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THE MOLECULAR WEIGHT AND CONSTITUTION OF NATURAL RUBBER *

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As is well known, crepe rubber is prepared from freshly gathered latex by the addition of dilute formic acid, and it contains natural rubber hydrocarbon in unaltered or but slightly altered form. Some years ago Meyer and Mark¹ measured the osmotic pressure of crepe rubber in benzene. At that time the authors based their calculations on an equation derived from the hypothesis that the system was solvated. However, this deduction can no longer be considered valid, for rubber is not solvated in benzene or in toluene, as has been proved

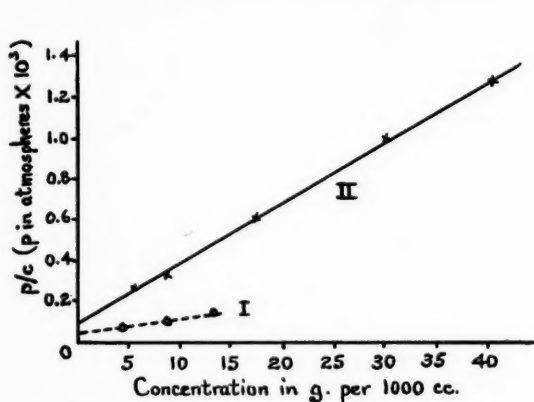


FIG. 1.—Reduced osmotic pressures (p/c) of crepe rubber (Curve I) and slightly masticated rubber (Curve II).

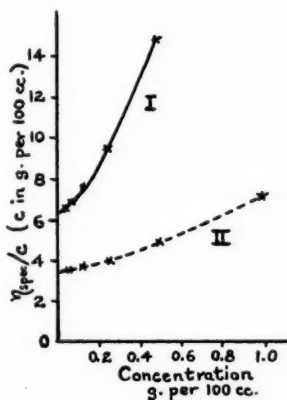


FIG. 2.— η_{spec}/c as a function of the concentration of crepe rubber (Curve I) and slightly masticated rubber (Curve II).

recently by Meyer, Wolff and Boissonnas² by the fact that solution is accompanied by a slight absorption of heat.

In view of this, these earlier results should be evaluated graphically so that the reduced osmotic pressures, p/c , are extrapolated to zero concentration (see Figure 1 and Table I). When evaluated in this way, the limiting value of p/c of 0.5×10^{-3} atmospheres, corresponding to a molecular weight of approximately 500,000, is obtained.

The limiting viscosity $c \xrightarrow{\lim} 0 \left[\frac{\eta_{\text{spec}}}{c} \right]$ of crepe rubber was determined, and this value was compared with that of a rubber slightly degraded by mastication, the molecular weight of which had been previously determined by the osmotic method² (see Figure 2 and Table I).

In this work, a mixture of 91 volumes of toluene and 9 volumes of butanol

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was employed, which dissolves rubber more rapidly and gives a more nearly homogeneous solution than does an apolar solvent, such as toluene alone. Natural rubber (crepe and latex) does not dissolve completely in pure solvents; aside from the viscous solution which is obtained, a transparent gel or a mass of swollen particles is formed. This is the gel rubber of Pummerer. When a small proportion of butanol is added to the apolar solvent, the gelatinous part dissolves, as is well known to rubber technologists. A similar phenomenon was observed by Pummerer, Kröpelin and Miedel³, who showed that this gel rubber dissolves when an aliphatic amine is added to the pure solvent.

TABLE I

OSMOTIC PRESSURES OF MASTICATED RUBBER

(Sample No. 2 in Toluene; Temperature 24.5° C; p in Atmospheres—Data of Meyer, Wolff and Boissonnas²)

Concentration (c grams per liter)	Pressure ($p \times 10^3$)	(p/c) $\times 10^3$	Molecular weight
5.63	1.46	0.26	270,000 \pm 10%
8.85	2.90	0.328	
17.6	10.75	0.612	
30.2	30.15	1.00	
40.4	51.5	1.27	

OSMOTIC PRESSURE OF CREPE RUBBER

(In Benzene; Temperature 7° C; p in Atmospheres—Data from the Literature¹⁰)

Concentration (c grams per liter)	Pressure ($p \times 10^3$)	$p/c \times 10^3$	Molecular weight
4.3	0.36	0.084	500,000 \pm 10%
8.7	0.94	0.11	
12.9	2.05	0.16	
4.3	0.36	0.084	500,000 \pm 10%
8.7	0.94	0.11	
12.9	2.05	0.16	

The cross-bonds which hold the gel together cannot be chemical bonds because of the ease with which they are ruptured by addition of a polar solvent. It may

be concluded that rubber contains a small proportion of $\begin{array}{c} | \\ \text{C}=\text{O} \\ | \end{array}$, $\begin{array}{c} | \\ \text{C}-\text{OH} \\ | \end{array}$ or $\begin{array}{c} | \\ \text{COOH} \\ | \end{array}$ groups, which exist in the natural state, or are formed as a result of secondary reactions. These groups can become associated in an apolar medium, and they are ruptured by the action of a dipolar reagent such as an alcohol:



Similar association phenomena are manifest even in homogeneous solutions of rubber in apolar solvents. In recent work, Staudinger and Fischer⁴ have proved that the viscosities of different samples of rubber are far from being proportional to their molecular weights. These authors attribute such disproportionalities to more or less pronounced branchings of the rubber chains. On the contrary, the present authors are of the opinion that these phenomena are the result of associations of the kind described above.

In making the viscometric measurements (by means of an Ostwald vis-

cometer), the solutions were filtered through a fritted-glass filter, Type 3-G2. When the solutions were protected from light, their viscosities remained constant for three weeks.

In Table II, K_m equals the limiting viscosity divided by ten times the degree of polymerization.

The data in Table II demonstrate that the relation of Staudinger for chain polymers is valid, *i.e.*, the limiting viscosity is proportional to the molecular weight. This relation has been found to be true in many cases of neighboring

TABLE II

	Limiting viscosity in-toluene- butanol	Molecular weight	Degree of polymeriza- tion	$K_m \times 10^4$
Rubber slightly masticated.....	3.3	270,000	4000	0.82
Crepe rubber	6.3	500,000	7300	0.86

TABLE III

VISCOSITIES OF SOLUTIONS OF RUBBER AT 25° C

Rubber and molecular weight	Concentration (grams per 100 cc.)	Relative viscosity (η_{rel})	Specific viscosity (η_{spec})	Ratio η_{spec}/c
Crepe approximately 500,000 (Solvent: toluene-butanol 91:9)	0.5	8.37	7.37	14.7
	0.25	3.33	2.33	9.3
	0.125	1.935	0.935	7.5
	0.0625	1.41	0.41	6.55
	0.0312	1.20	0.20	6.4
	→0	—	—	6.3
Masticated rubber approxi- mately 270,000 (Solvent: toluene-butanol 91:9)	1.0	7.95	6.95	6.95
	0.5	3.41	2.41	4.82
	0.25	1.98	0.98	3.92
	0.125	1.44	0.44	3.52
	0.0625	1.208	0.208	3.33
	→0	—	—	3.25
Masticated rubber (English sheet) (Solvent: toluene- butanol 91:9)	0.0842	1.34	0.34	4.0
	→0	—	—	3.8
Masticated rubber approxi- mately 270,000 toluene (Solvent: toluene)	0.082	1.333	0.333	4.1
	0.041	1.16	0.16	3.9

members of a series of homologous polymers. This subject will be dealt with at a later time.

The viscosities in the solvent used in the present experiments were 20 per cent lower than those in toluene (see Table III). The addition of butanol, therefore, lowers the relative viscosity of rubber.

The molecular weight of *Hevea* rubber is, then, approximately 500,000. Kröpelin and Brunshagen⁵ obtained values similar to this, and Kraemer and Lansing⁶ obtained values of 400,000 to 435,000 by ultracentrifuging raw rubber soluble in ether.

In the present work, in addition, the viscosity of a commercial rubber (English sheet) was determined. This rubber showed a molecular weight of 350,000.

CONSTITUTION OF RUBBER

As stated by Weber⁷ and by Pickles⁸, rubber is composed of long chains. In studies of x-ray spectra, Meyer and Mark⁹ proved that rubber must be regarded as having a *cis* form and not a *trans* form, as still believed today by Staudinger. In a recent publication, Staudinger and Fischer claim to have proved that native rubber is not composed of straight chains but of branched chains; in fact, according to Staudinger all polymers with simple unbranched chains follow the "viscosity law", i.e., the reduced specific viscosity in dilute solution, η_{spec}/c , is proportional to the molecular weight, and the quotient $\eta_{\text{spec}}/(cM)$ is a constant (the constant K_m). The K_m value of rubber is not a constant, but diminishes in proportion to the increase in molecular weight. This is the reason that Staudinger rejects an unbranched chain structure of rubber.

To verify this view of Staudinger, it is necessary to prove first of all that η_{spec}/c is proportional to the length of chain. A considerable mass of data is

TABLE IV

Solution	The K_m value diminishes	
	From	To
Methyl ester of polymethylacrylic acid in acetone.....	0.56	0.19
Polystyrene in toluene.....	0.56	0.19
Methyl ester of polyacrylic acid in acetone.....	0.45	0.31
Polyvinyl acetate in acetone.....	0.52	0.25
Polyvinyl alcohol in water.....	0.68	0.43
Polyvinyl chloride in tetrahydrofuran.....	1.05	0.54

TABLE V

Molecular weight of cellulose	$K_m \times 10^4$
2000.....	14.2
4400.....	12.6
18000.....	11.5
30200.....	9.3
51200.....	8.6
103300.....	7.7

available, but is inexact to a great extent; it shows only that the reduced viscosity is a continuous, increasing function of the chain length. The graph of this relation is only slightly curved, and appears to be a straight line within a limited region. With neighboring members of an homologous series, the viscosity is roughly proportional to the molecular weight. However, if a more extended region of the curve is considered, i.e., if homologs whose molecular weights differ by one or several orders of magnitude are compared, it is found that in all cases the K_m value diminishes with increase in the molecular weight.

Staudinger and Fischer¹⁰ have proved this fact for the compounds given in Table IV.

In the case of higher polymers, the quotient η_{spec}/c is ordinarily less than one-half that of their lower homologs.

An identical phenomenon is to be found in the case of cellulose and triacetylcellulose. Here the K_m values of cellulose in Schweitzer solution diminish with increase in the molecular weight, as is evident from the values in Table V, which were obtained by Staudinger¹¹.

The same is true of triacetylcellulose in *m*-cresol. According to Staudinger and Daumiller¹², the viscosity/molecular weight quotient is 20×10^{-4} for the lower homologs; it falls to 6.3×10^{-4} for homologs with a degree of polymeriza-

tion of 100, and it is only 3.3×10^{-4} for homologs with a degree of polymerization of 2000, as Lachs and Grosman¹³ have been able to demonstrate in an extensive investigation.

Rubber behaves exactly like other polymers with high molecular weights and unbranched chains, for in toluene the K_m value of the lower homologs of poly-prene is 3.8×10^{-4} , whereas the K_m value of the higher homologs is 1×10^{-4} (see the table of Staudinger and Fischer¹⁴). Hence there is no reason to suppose that rubber has a branched chain structure.

The ratio of the viscosity to the concentration is another factor which speaks in favor of the unbranched chain structure. The empirical relation of Fikentscher applies in an approximate way to polymers with unbranched chains:

$$\log \eta_{rel} = \left(\frac{75k^2}{1 + 1.5kc} + k \right) c$$

where η_{rel} is the relative viscosity at concentration c , c is in grams per 100 cc., and k is the parameter of the curve which is designated by characteristic viscosity (see Table VI).

TABLE VI
CHARACTERISTIC VISCOSITY
(Eigenviskosität of Fikentscher)

	Concentration (g. per 100 cc.)	η_{rel}	$K \times 10^3$
Masticated rubber (in toluene).....	0.5	3.41	117
	1.0	7.95	111
Crepe ¹⁵ (in chlorobenzene)	0.5	9.75	165
	1.0	44.9	158
	1.5	183.0	156
	2.0	622.0	156

In view of the fact that rubber likewise conforms to this law, as has been proved by Fikentscher¹⁵ and as the present authors have been able to confirm, it is not necessary to assume a branched-chain structure of rubber.

On the other hand, it is not at all impossible that some of the degradation products and transformation products of rubber have branched-chain structures. Rubber can, for example, be condensed by the action of ultraviolet radiation, by iodine in conjunction with visible light¹⁶, and by oxygen. The polymers which are obtained by these means have reticulated structures, and can swell only to a limited degree, but on the other hand, they can be degraded further into smaller molecules which have branched-chain structures.

RÉSUMÉ

Natural rubber is composed of unbranched chains, with a molecular weight of 400,000 to 500,000. Condensation reactions, i.e., bridge linkings, and degradation reactions may result from subsequent treatment, and in this way molecules with branched chains may be formed.

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THE OPTICAL PROPERTIES OF RUBBER *

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INTRODUCTION

The potentially extensive field of research embracing the optical properties of rubber, in comparison with the study of its mechanical, thermal, and electrical properties, has been relatively neglected. It is possible, therefore, even within the limits of the present paper, to give a fairly complete general survey of this field, with brief indications of theoretical consequences and practical applications, as well as some possibilities for future research. Principal consideration is given to four optical properties—absorption, scattering, refractive index, and double refraction. Previous work on each of these topics is summarized and, in the case of absorption and refractive index, the results of hitherto unpublished measurements made at the National Bureau of Standards are included. No discussion is given regarding the microscopy of rubber, since the topic is complex and somewhat distinct from those treated here.

ABSORPTION

The transmission of light by a material is a property of fundamental importance in the study of almost any of its optical properties. Purified rubber hydrocarbon, like all other hydrocarbons, with a few exceptions, has been found to have no absorption bands in the visible region of the spectrum. Consequently this material appears colorless and transparent. Commercial raw rubber, on the other hand, possesses a distinctly amber or orange-yellow color. The color is readily evident in rubber prepared by drying latex or by coagulating latex and drying the coagulum, after washing. In smoked sheet the natural color is also evident, although darkened by components of the smoke. In pale crepe, on the other hand, it is usually obscured by the white appearance arising from minute air bubbles or tiny surface irregularities, but is readily noticeable after milling.

Since measurements of the transmission of rubber as a function of wavelength do not seem to have been reported, the results of unpublished measurements made at the National Bureau of Standards, using the General Electric automatic recording spectrophotometer, are included here. Data on six specimens of different thickness are shown in Figure 1. The solid curves are for milled 1-X pale crepe, and the broken curves for a vulcanized compound made from it. In all cases the data have been corrected by the usual relation for reflection at the surfaces. This relation, based on theoretical considerations, assumes that the ratio of intensities of reflected and incident beams at each surface is equal to $(n-1)^2/(n+1)^2$, where n is the refractive index of the material. In the computation, use was made of the values of the refractive index given in a later section. In all but one case the corrections amounted to between 8 and 9 per cent of the observed values.

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These curves should not be regarded as possessing any absolute significance, especially since the absorption seems to be caused by an impurity and not by rubber hydrocarbon itself. The transmission and color of raw rubber vary considerably from one bale to another, as every rubber technologist knows. The color of a vulcanized compound also depends on the nature and amounts of vulcanizing ingredients, particularly the accelerators. The results are, however, typical of the transmission which can be obtained from unpurified, commercial rubber.

If one calculates from the data values of the apparent absorptive index at a given wave-length, the magnitude of the apparent index is found to decrease with increasing thickness of the specimen. From this fact one would conclude that there are surface effects which diminish the intensity of the transmitted beam, and which are, of course, relatively less important with the thicker speci-

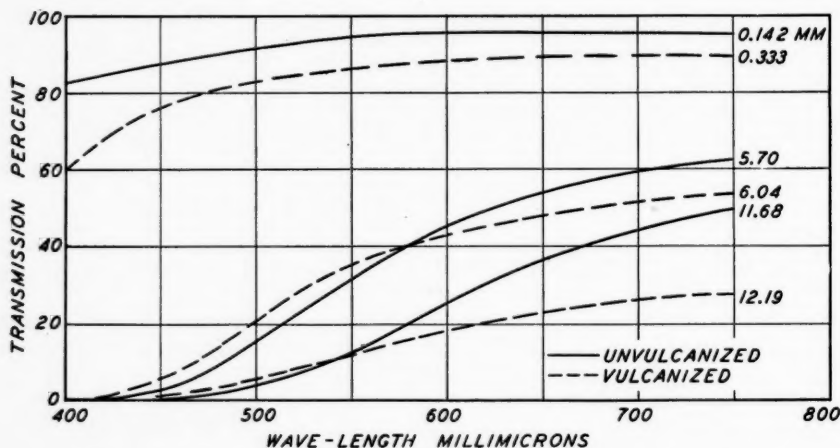


FIG. 1.—Transmission of specimens of different thickness as a function of wave-length.

mens. Such effects were not noted by Hock and Müller¹⁰, in observations with red light on specimens ranging from 1.3 to 5.4 mm. in thickness.

According to the work of Eaton and Fullerton⁸, the pigment responsible for the color of raw rubber is the yellow hydrocarbon carotene²³ (one of the exceptions to the general rule previously mentioned). They found the amount of carotene in most samples of rubber to be only of the order of 0.002 per cent. Bondy and Lauer⁵ have found strong antioxidant activity in the presence of light, either in the pigment itself or in some material which they could not separate from it. They found, however, that carotene from other sources showed no antioxidant activity.

The crystallization of a sheet of rubber is found to reduce the transmission very considerably⁴³, and to give the sheet a white appearance. These effects are presumably caused primarily by the heterogeneity of the mixture of amorphous and polycrystalline material, and not necessarily by an absorption within each crystal.

The transmission of the vulcanized specimens, shown by the broken curves, shows the same general features as that of the unvulcanized ones. However, for specimens of nearly the same thickness, a crossing of the curves is evident.

For the particular compound used, vulcanization actually increased the transmission at the shorter wave-lengths, while decreasing it at the longer. The specimens therefore appear a greenish-yellow, while the raw rubber from which they were made is distinctly more orange-yellow. It is not obvious whether the increased transmission at the shorter wave-lengths is the result of some chemical reaction of the pigment during vulcanization or of some other cause.

In compounding rubber to obtain a vulcanizate of high transmission, it is desirable to add only enough compounding ingredients to obtain good vulcanization, avoiding especially any excesses of materials which might crystallize out. To keep the sulfur content low, an "ultra-accelerator" is almost invariably used. In our work it has been found desirable to use rather low temperatures of vulcanization, with correspondingly lengthened times.

The transmission curves in Figure 1 were obtained in experiments on vulcanizates of the compound given in Table I.

Fillers having nearly the same refractive index as rubber may be incorporated into a compound in considerable volume without impairment of the transmission. Magnesium carbonate, the best-known example of such a filler, has been studied by several observers^{3, 4, 37}. In amounts up to 15 per cent, the addition

TABLE I

	Parts by weight
Pale crepe No. 1-X.....	100
Sulfur	1.5
Tetramethylthiuram monosulfide	0.188
Zinc oxide (Kadox).....	0.5
Acrin	0.5
AgeRite Gel	0.25
Total	102.938

Vulcanization: 90 minutes at 103° C

of one variety of the carbonate actually increased the transmission. This effect was ascribed to the dilution of the rubber by the carbonate, which has a relatively higher transmission.

The ultraviolet absorption of purified rubber in solution has been studied^{22, 28, 34}, and no appreciable absorption is found at wave-lengths longer than about 270 m μ . Below this point the absorption increases, and becomes very strong at about 200 m μ . The increase of absorption appears to be uniform, without the superposition of any observable fine structure. Somewhat similar results have been obtained with thin films of rubber^{2, 21}.

The infrared absorption of rubber has been measured by a number of investigators^{6, 35, 45-47}. Since the subject is being discussed by Sears in another paper³⁰, it needs merely be stated here that a number of absorption bands have been found, and some of them have been identified in terms of atomic vibrations. No absorption bands have been observed at wave-lengths shorter than 2 μ .

SCATTERING

It can be observed that light is scattered very considerably in its passage through rubber. A considerable portion of the decreased transmission of rubber at shorter wave-lengths is caused by scattering rather than by actual absorption by a pigment. The nature of the particles responsible for the scattering has not been established.

Some idea of the magnitude of the scattering at different wave-lengths may be gained from Figure 2. The upper curves *U* and *V* are the curves already shown in Figure 1 as the values of the transmission of unvulcanized rubber 5.70 mm. thick and of the vulcanized rubber 6.04 mm. thick. The optical system, as with all the measurements already discussed, was such that light scattered by the specimen at angles as large as about 38° with the axis was included and measured as transmitted light. When the specimens were moved farther away from the collecting aperture, so that only light making angles of about 8° or less with the axis was included in the measurement, the lower curves, *U'* and *V'*, were obtained. In the former position a considerable amount of scattered light was included, since the solid angle subtended was about 20 per

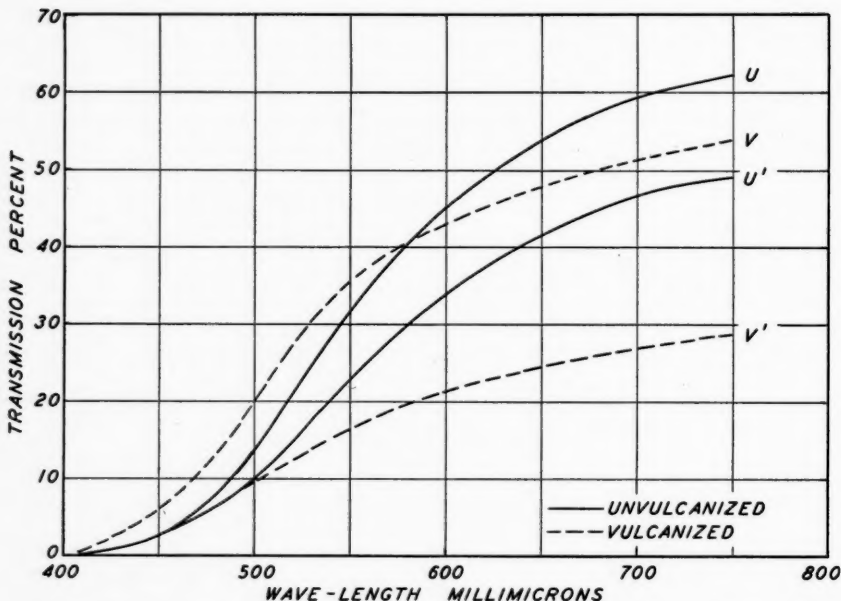


Fig. 2.—Transmission as affected by scattering. For curves *U* and *V*, light scattered at all angles less than about 38° with the incident beam was included. For curves *U'* and *V'*, light scattered at all angles less than about 8° with the incident beam was included.

cent that of a full hemisphere. In the latter position relatively little scattered light was included, since the solid angle subtended was about one per cent that of the hemisphere. Some indication of the amount of light scattered at angles less than 38° , then, may be obtained from the difference in ordinates of the corresponding curves *U* and *U'*, and *V* and *V'*. The values obtained vary somewhat with wave-length, but are of the order of one-third that included in the direct beam, in the case of the unvulcanized rubber. For vulcanized rubber, the scattered light is very approximately equal to that in the direct beam. The larger scattering in the vulcanized rubber is probably caused by the presence of uncombined, undissolved compounding ingredients.

Some observations regarding the effect of stretching on the scattering of light in rubber have been made by Schwarzenbach²⁹. He discovered several striking optical effects, which are as yet unexplained. A beam of light, circular in cross-

section, was found to be scattered by stretched rubber in such a way that the section was no longer circular, but consisted of several crossed bands of light.

The scattering of light by rubber solutions has been the subject of extensive studies by Gehman and Field¹⁰⁻¹². In other work¹³ the scattering of light by filler particles in rubber has been made the basis of a method of measuring their size.

The Raman effect—the change of wave-length on scattering—has been the subject of several investigations dealing with rubber solutions. A number of characteristic frequencies were observed by Gehman and Osterhof¹⁴, and some were identified in terms of the atoms involved. Reasonable agreement between these results and those obtained from infrared absorption bands was obtained in several cases.

REFRACTIVE INDEX

Of all the optical properties of rubber, the refractive index has probably received the most attention²⁵. In fact it seems to be the only optical property of the different varieties of synthetic rubber which has been discussed in the literature⁴⁹. For natural rubber, its value is found to depend but little on the origin, preparation, or purification of the rubber. Most observers^{19, 24} have used the Abbé or the Pulfrich refractometers to measure the index. These instruments, although convenient and rapid in operation, depend on measurement of the critical angle of total reflection, and are inherently somewhat less precise and accurate than the best spectrometers. Accordingly in some work, as yet unpublished, at the National Bureau of Standards, a number of rubber prisms were made for use with a spectrometer. Complete details of their construction are included in a paper which is now in preparation.

Pale crepe rubber was milled and moulded against small plates of glass, the effective surfaces of which were optical plane parallels. For vulcanized rubber prisms, two compounds were employed, one containing about 1.5 per cent sulfur and the other about 1.9 per cent sulfur, with accelerators and other ingredients in very small amounts. The specimens were moulded or vulcanized, as the case might be, in the form of prisms having refracting angles of about 10° in some cases and about 20° in others. The glass plates were not removed, but their presence did not alter the direction of the light beam, since they were optically plane parallel, as determined by a method involving the interference of light from the two surfaces. The glass plates served to keep the rubber surfaces clean, and to prevent distortion of the rubber.

Measurements of the angles of minimum deviation for light refracted by these prisms were made, in coöperation with L. W. Tilton, by the use of a spectrometer in the usual manner. The refracting angles of the prisms were measured with the spectrometer and, from these data, refractive indices could be calculated. Measurements were made at five different wave-lengths, corresponding to the *C*, *D*, and *F* lines of Fraunhofer, as well as the *e* and *g* mercury lines. The light sources were a mercury arc, a hydrogen discharge tube, and a sodium flame. Measurements were made at several temperatures, the temperature coefficient thereby determined, and the results finally computed at a standard temperature at 25° C. The results are shown in Figure 3. The curve for ordinary crown glass is given for comparison.

The dispersion, defined as the difference between indices at two arbitrary wave-lengths, usually the Fraunhofer *F* and *C* lines of the hydrogen spectrum, is seen to be somewhat higher for rubber than for the glass. Its value for unvul-

canized rubber at 25° C is 0.01315. This is not far different from that found for unconjugated diolefin hydrocarbons of low molecular weight⁴⁴.

The results show good agreement with the measurements of previous observers, who with a single exception obtained values of the index only for the sodium *D* line. McPherson and Cummings²⁴, studying an extensive series of rubber compounds vulcanized with sulfur alone, have shown that the refractive index increases by 0.0037 for each per cent of combined sulfur. Assuming the continued validity of this result when accelerators are employed, one may con-

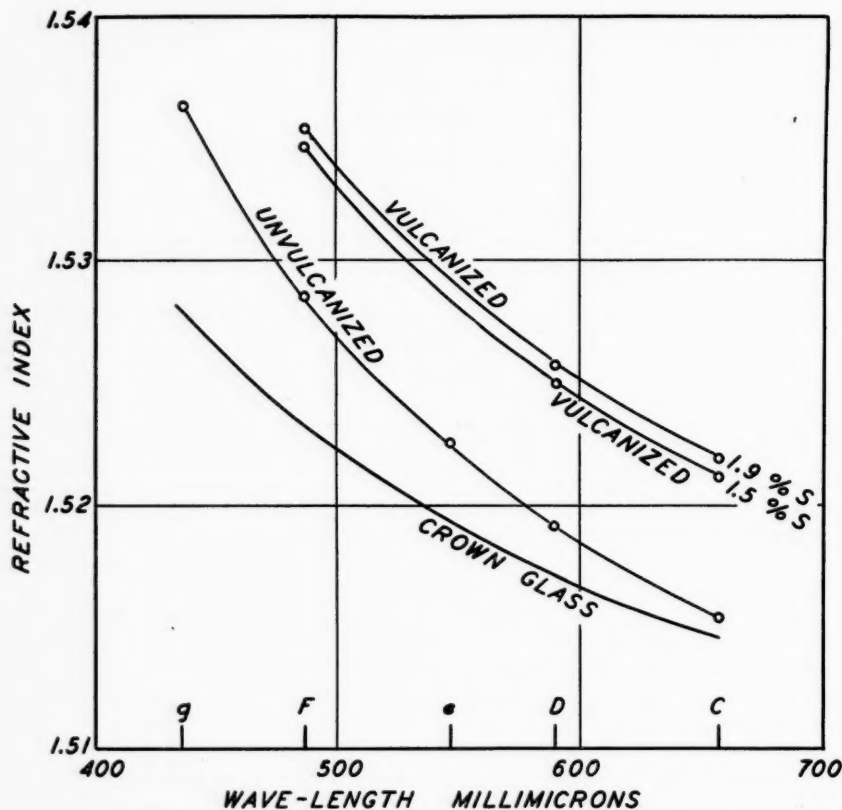


FIG. 3.—The variation of refractive index at 25° C with wave-length.

clude that 1.6 per cent and 1.9 per cent of combined sulfur are present in the two specimens of vulcanized rubber. There is good correspondence between these values and the 1.5 per cent and 1.9 per cent used in the compounds. It is to be expected that, under the conditions of the experiment, practically all of the sulfur would become combined.

It is common practice to calculate the molecular refractivity *R* from the refractive index *n_D*, density *ρ*, and molecular weight *M*, of a substance. The formula usually used is that of Lorenz and Lorentz, namely:

$$R = \frac{n_D^2 - 1}{n_D^2 + 2} \frac{M}{\rho}$$

It is found that for many organic compounds, particularly hydrocarbons, the molecular refractivity is an additive function of terms called atomic refractivities, depending on the nature of the atoms and bonds present. The values of the atomic refractivities given by Eisenlohr⁹ were based on studies of a great number of compounds, and have been extensively used. More recent work has led to the suggestion of somewhat different values for the atomic refractivities of carbon and hydrogen, but not to any new value for the refractivity to be associated with a double bond. By the use of Eisenlohr's value, 1.733, for the refractivity to be associated with the double bond, and the various suggested values for the atomic refractivities of carbon and hydrogen, the values of molecular refraction of a C_5H_8 unit containing one double bond have been calculated. The following results were obtained, corresponding to the values for the atomic refractivities suggested by the respective authors: Eisenlohr⁹, 22.62; Swientoslawski²⁶, 22.71; van der Hulst⁴¹, 22.88; and Alsopp and Willis¹, 22.65. All of these are in sufficiently good agreement with the experimentally determined value of 22.82 to afford optical confirmation of the chemical observation of the existence of a C_5H_8 unit containing one double bond, as the unit group in rubber.

The incorporation of coarse filler particles in rubber, although usually accompanied by a diminution in light transmission, is found to be without influence on the refractive index. Zinc oxide and whiting, however, when present in rubber as particles a few tenths of a micron in diameter, or smaller, are found to raise the value of the refractive index. This effect was first observed by McPherson and Cummings²⁴ and further investigated by Jones¹⁷. Its explanation is probably closely associated with the fact that the size of the particles involved is smaller than the wavelength of the light used.

The refractive index of mixtures of unvulcanized rubber and sulfur has been found by McPherson and Cummings²⁴ to bear a linear relation to the amount of sulfur, with an increase in index n_D^{25} of 0.0016 for each per cent of sulfur. The measurements in this case were taken within an hour after mixing on a hot mill. Measurements on mixtures containing up to 4 per cent of sulfur were made one month and fourteen months later. They reproduced the first measurements only up to an index corresponding to 1.2 per cent of sulfur. Above this point, the index in the later measurements showed no further increase. This effect was ascribed to the presence of a supersaturated solution of sulfur in rubber during the first observations. Crystallization of the excess sulfur had occurred during the interval of a month between the first set and the second set of observations. The value 1.2 per cent, for the amount of sulfur in a saturated solution in rubber at 25° C, is in very good agreement with that very recently obtained by Kemp and his coworkers¹⁸ in an extended investigation by a method involving direct visual observation of the crystallized sulfur. Observations of refractive index can be utilized in a similar manner to measure the solubility of other compounding ingredients in rubber provided that the refractive indices are appreciably different from that of rubber. The solubility of phenyl-beta-naphthylamine is found by this method to be also 1.2 per cent at room temperature²⁴.

DOUBLE REFRACTION

Rubber appears to be normally isotropic, and the speed of light in it is normally the same in all directions. When it is stretched, however, this is no longer true, and double refraction occurs. A beam of light passing through it emerges as two plane-polarized rays, the ordinary and extraordinary rays. The velocities

of these rays, as evidenced by the corresponding indices of refraction, differ, so that there is a phase difference between the rays as they emerge. The amount of phase difference, or retardation of one ray with respect to the other, has been shown by Thibodeau and McPherson³⁸ to be usually proportional to the thickness of the rubber and to the stress, provided that the stress is uniform over any section of the sheet, and shearing stresses are absent. The proportionality constant is the stress-optical coefficient. The value found for the stress-optical coefficient of soft vulcanized rubber is about 2100 brewsters, a brewster being 10^{-13} sq. cm. per dyne. Most other materials⁷ have stress-optical coefficients below 50 brewsters. Gelatin apparently is the only material for which values higher than that of rubber have been reported. The retardation is usually measured by means of the arrangement of displaceable quartz wedges commonly known as the Babinet compensator. It is found that the ordinary ray is faster than the extraordinary ray, and is polarized, so its vibrations are at right angles to the direction of stress^{20, 27}.

Double refraction may be used as a means of evaluating the actual stresses in rubber, when it is difficult to measure them directly. In this manner structural changes during the processing of rubber have been studied¹⁵, and the complex stresses around a rigid inclusion have been evaluated³⁹.

The double refraction thus far discussed is similar to that observed with many noncrystalline materials, and has been considered to have no connection with crystallization of the rubber. The conditions that double refraction is present at low elongations and that it bears a linear relation to stress do not correspond to those involved in the formation of crystals, as studied by other methods of observation. However, if the conditions are such that crystals of rubber are formed, a crystalline double refraction appears, and may be superimposed on that caused by stress alone.

One method of inducing the formation of crystals is by stretching the rubber. Elongations of at least 100 per cent are found to be required. The crystals in this case have one direction fixed, and a fiber axis is found along the direction of stretching. There is random orientation of the crystalline axes in the plane at right angles to this axis. Double refraction has been used in conjunction with a parallel study by x-rays to investigate the conditions of formation of crystals in stretched rubber^{26, 40, 42, 48, 50}.

Unstretched rubber may be crystallized also at temperatures from about 15°C to -40°C , or at room temperature at pressures greater than atmospheric. The crystals which are formed in this manner are usually, if not always, very small and oriented at random³². The crystals are not isotropic, and double refraction occurs in each crystal^{31, 33}. Because of the random orientation, it is often impossible to make quantitative measurements of double refraction in this case. However, if the rubber is crystallized from solution^{31, 33} or from very thin films formed by evaporation of a rubber solution³², it is sometimes possible to obtain needle-like single crystals which may be observed under the microscope. From crystals obtained in this manner, ϵ and ω , the two refractive indices corresponding to vibrations along and at right angles to the axis of a uniaxial crystal, respectively, were determined at -5°C . The values obtained^{31, 33} were $\epsilon = 1.535$ or 1.533 , and $\omega = 1.583$.

CONCLUSIONS

The general survey which has been presented here shows that, while a number of the optical properties of rubber have been investigated, the measurements

of most of them have been more or less preliminary or exploratory in nature and often directed towards some immediately practical application. There appears to be ample opportunity for extended, systematic research on the optical properties for their own sake.

The results to be expected from such study may lead in two directions, each of them illustrated in a very preliminary fashion, by examples given in the present paper. The one direction is that of more fundamental knowledge of the constitution of rubber, especially when optical methods are used in conjunction with other types of measurement. An illustration already mentioned is the use of molecular refractivity to confirm the existence of a C_5H_8 unit containing one double bond as the unit group in rubber. Such work might well be extended as assistance in elucidating the constitution of vulcanized rubber. Another illustration is the use of infrared spectra or Raman spectra to determine the types of chemical bonds present in rubber.

The other direction in which a study of the optical properties of rubber may lead is toward the direct solution of practical problems without regard for the theoretical significance of the measurements. Problems of control or analysis might be approached in this manner, since optical methods usually require only small amounts of material, and are often easily adaptable to rapid and precise measurements. Such applications have already been illustrated in preliminary form by the use of refractive index to determine amounts of combined or dissolved sulfur. The solution of practical problems by optical methods is also illustrated by the use of the photoelastic method for the analysis of stresses in rubber.

Optical measurements in the past have been restricted in most cases to samples having fairly high light transmission. On this account the work has included only unvulcanized rubber and vulcanized compounds of the "pure gum" type. By the use of very thin sections or by employing methods which are based on the reflection of light rather than its transmission, it should be possible to extend the measurements to many practical rubber compounds which appear to be opaque, but which in reality are dispersions of filler particles in a matrix of transparent rubber.

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HYDRODEPOLYMERIZATION OF RUBBER *

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In a previous paper¹, one of the authors showed that the thermal decomposition of both natural and synthetic rubber proceeds easily and rapidly in the presence of aluminum chloride. The product so obtained is a mixture of hydrocarbons particularly rich in cyclic forms. One might, therefore, be led to believe that the polymerization of isoprene or butadiene, both in nature and under synthetic conditions, may be preceded by their dimeric or polymeric cyclization, with subsequent association of these unsaturated cyclic compounds, resulting in the formation of rubber.

As a contribution to the knowledge of the chemical nature of highly polymeric substances such as rubber, we present here the results of our investigations on the depolymerization of rubber when subjected to hydrogen under high pressure in the presence of a catalyst. It was found that rubber, in the same way as oil or coal tar, is completely liquefied under such conditions. Experiments showed that, within the relatively short time of 1.5 to 2 hours, at a temperature of 400° C and a hydrogen pressure of 150 atmospheres, and in the presence of molybdenum sulfide or of nickel deposited on aluminum oxide, rubber is completely converted into a mobile liquid consisting of saturated and unsaturated hydrocarbons. The chemical nature of the resultant hydrocarbons casts light on the structure of rubber. It should be noted here that, in the absence of a catalyst, rubber cannot be converted into a mobile liquid when subjected to hydrogen under pressure.

I. EXPERIMENTS WITH NATURAL RUBBER

One hundred grams of natural rubber (pale crepe), containing 95.8 per cent of pure hydrocarbon, were introduced into an autoclave, with 4 per cent of molybdenum sulfide as catalyst. The initial hydrogen pressure was 80 atmospheres, and the temperature was raised slowly to 400° C. The entire experiment was completed in 2.5 hours, and 95 grams of a mobile oil of pleasant odor were obtained. In this case 2.02 per cent of hydrogen (based on the original charge of rubber) were used up in the reaction. In a second experiment a 200-gram charge was used, and 194 grams of the same product were obtained. In this case 2.05 per cent of hydrogen took part in the reaction. The two experiments gave a total yield of 289 grams of hydrodepolymerization product. This was markedly unsaturated, and had a refractive index n_D^{25} of 1.4800. For purposes of preliminary classification, 200 cc. of the product were subjected to fractional distillation:

1st fraction.....	40-100° C	20 cc.	$n_D^{24} = 1.3950$
2nd fraction.....	100-150° C	20 cc.	$n_D^{24} = 1.4340$
3rd fraction.....	150-200° C	50 cc.	$n_D^{24} = 1.4580$
4th fraction.....	up to 175° C (22 mm.)	58 cc.	$n_D^{24} = 1.4896$
5th fraction.....	175-295° C (22 mm.)	40 cc.	$n_D^{24} = 1.5149$

The last fraction was fluorescent.

* Translated by J. Talalay for RUBBER CHEMISTRY AND TECHNOLOGY from the *Bulletin of the Academy of Sciences of the U. S. S. R., Division of Chemistry*, 1940, No. 5, pages 681-689.

Judging from the high refractive indices, the rubber had been decomposed into hydrocarbons containing a large proportion of cyclic compounds of both saturated and unsaturated nature.

A third experiment was performed under identical conditions of temperature and pressure, except that in this case 5 per cent of a catalyst consisting of nickel deposited on aluminum oxide was used.

Two hundred grams of rubber gave a yield of 196 grams of a mobile oil with a pleasant odor. In this instance, the amount of hydrogen consumed was 2.3 per cent of the weight of the initial rubber charge.

An analysis of the gaseous products of the decomposition showed:

CO ₂	0.43 grams	0.21 per cent
CO	0.36 grams	0.18 per cent
Hydrocarbons of the methane group.	3.63 grams	1.81 per cent

The experiment, using nickel as a catalyst, was repeated with an initial hydrogen pressure of 90 atmospheres and a gradually rising temperature: 30 minutes at 300° C, 30 minutes at 350° C, and 1.5 hours at 380-400° C.

In both instances, a liquid product free of any residue was obtained. Altogether, 400 grams of rubber yielded 389 grams of depolymerized product. The refractive index n_D^{25} of 1.4591 was substantially lower than in the previous experiments with molybdenum sulfide as catalyst.

To compare the results with those of the previous series (molybdenum sulfide catalyst), 350 cc. of the product was subjected to fractional distillation:

1st fraction.....	45-100° C	46 cc.	$n_D^{25} = 1.3880$
2nd fraction.....	100-150° C	49 cc.	$n_D^{25} = 1.4250$
3rd fraction.....	150-200° C	92 cc.	$n_D^{25} = 1.4521$
4th fraction.....	up to 240° C (22 mm.)	133 cc.	$n_D^{18} = 1.4830$
5th fraction.....	220-290° C (5 mm.)	22 gram	$n_D^{18} = \dots$

To ascertain the nature of the hydrocarbons contained in the fractions resulting from hydrodepolymerization of rubber, individual fractions were united and subjected to catalytic hydrogenation at atmospheric pressure in contact with platinized, active carbon. In this way the unsaturated compounds in the depolymerized product, among which there might also be unsaturated derivatives of cyclohexane, were converted into completely saturated hydrocarbons. In these latter, the corresponding aromatic compounds could be determined quantitatively by means of catalytic dehydrogenation of all cyclic hexamethylene groups.

HYDROGENATION OF INDIVIDUAL FRACTIONS OF DEPOLYMERIZED RUBBER

The first and second fractions (40-150° C) were combined, and the portion boiling below 75° C was distilled off. The fraction 75-150° C, of n_D^{18} 1.4250, showed, after hydrogenation over platinized (20%) carbon at 160° C, a substantially lower refractive index ($n_D^{18} = 1.4161$), and exhibited fully saturated properties, giving no reaction with permanganate.

The third fraction (150-200° C) of n_D^{18} 1.4570 gave, after hydrogenation at 190° C in the presence of the same catalyst, again a considerably lower refractive index ($n_D^{18} = 1.4372$). No absorption took place when this fraction was treated with sulfuric acid (1.84).

From the fourth fraction, a portion boiling between 200 and 300° C at atmospheric pressure was separated. This had a refractive index n_D^{17} of 1.4830. After hydrogenation over platinized carbon at 210° C, a completely saturated product of refractive index n_D^{16} of 1.4720 was obtained.

From the higher boiling depolymerization product, a major portion boiling between 220° and 290° C at 5 mm. pressure was separated by distillation. A heavy, viscous oil was obtained ($n_D^{15}=1.5475$), which exhibited a pronounced fluorescence.

The completely saturated hydrogenation products were combined and fractionated within closer limits of boiling range. The aim was to subject the resulting individual fractions to catalytic dehydrogenation and, thereby, to decide how much richer in aromatic hydrocarbons any one fraction would become at the expense of the cyclic hexamethylene compounds. This made it possible to determine the aromatic content.

The entire hydrogenated material was divided into the following fractions:

1st fraction.....	up to 80° C	1.88 grams	$n_D^{19}=1.3816$
2nd fraction.....	80-100° C	9.00 grams	$n_D^{19}=1.4023$
3rd fraction.....	100-130° C	20.75 grams	$n_D^{19}=1.4130$
4th fraction.....	130-150° C	17.68 grams	$n_D^{19}=1.4240$
5th fraction.....	150-168° C	43.90 grams	$n_D^{19}=1.4340$
6th fraction.....	168-175° C	33.00 grams	$n_D^{19}=1.4398$
7th fraction.....	175-185° C	15.00 grams	$n_D^{19}=1.4428$
8th fraction.....	185-205° C	15.50 grams	$n_D^{19}=1.4579$
9th fraction.....	205-220° C	11.70 grams	$n_D^{19}=1.4618$
10th fraction.....	220-250° C	10.00 grams	$n_D^{19}=1.4700$
11th fraction.....	250-275° C	23.00 grams	$n_D^{19}=1.4761$

DEHYDROGENATION OF FRACTIONS DISTILLED FROM HYDROGENATED DEPOLYMERIZED RUBBER

Each fraction was subjected to dehydrogenation at 300° C over platinized active carbon. All fractions were treated in the presence of the same catalyst, without renewing it. To remove any aromatic compounds formed, the condensed dehydrogenation products were all treated with twice their volume of monohydrate or of Katwink's reagent, both procedures yielding identical results.

Dehydrogenation of the second fraction (80-100° C) yielded a condensate having a refractive index n_D^{24} of 1.4120, and a definite odor of benzene. On sulfonating 5 cc. of the product, 1.2 cc. was absorbed; from this it was deduced that 24 per cent by volume of aromatic substances (mostly benzene) were present.

Dehydrogenation of the third fraction (100-130° C) gave a condensate having a refractive index n_D^{23} of 1.4320. Sulfonating 10 cc. resulted in an absorption of 3.4 cc., which corresponds to 34.0 per cent of aromatic substances by volume (toluene and xylene). The residue, which could not be sulfonated, had a refractive index n_D^{25} of 1.3906.

The fourth fraction yielded, after dehydrogenation, a product of refractive index n_D^{23} 1.4465, and had a characteristic xylene odor. It was shown to contain 38.2 per cent of aromatic substances.

Dehydrogenation of the fifth fraction gave a catalytic product having a n_D^{23} value of 1.4611. The content of aromatic substances was high, viz., 54 per

cent. The unsulfonated residue had a refractive index n_D^{22} of 1.4220. The same procedure was applied to all the remaining fractions of the hydrogenated depolymerized rubber.

The sixth fraction gave a dehydrogenation product having a refractive index n_D^{23} of 1.4681. In this case, dehydrogenation was repeated. This, however, did not result in any appreciable increase in refractive index ($n_D^{23}=1.4687$), proving that a single dehydrogenation is sufficient. The catalytic product contained 60.0 per cent of aromatic substances (by volume). The unsulfonated residue had a n_D^{23} value of 1.4290.

7th fraction after dehydrogenation $n_D^{23}=1.4702$, aromatics 66 per cent
8th fraction after dehydrogenation $n_D^{25}=1.4720$, aromatics 66 per cent
9th fraction after dehydrogenation $n_D^{23}=1.4738$, aromatics 54 per cent
10th fraction after dehydrogenation $n_D^{24}=1.4780$, aromatics 53 per cent
11th fraction after dehydrogenation $n_D^{24}=1.4859$, aromatics 52 per cent

The unsulfonated residues from Fractions 5 to 11 were combined and treated with monohydrate to test for the presence of small quantities of aromatic substances. The test was negative, indicating that all aromatic hydrocarbons were removed from their respective fractions in the course of the sulfonation. The unsulfonated residue was washed, dried, and distilled in the presence of metallic sodium. It distilled over completely between 165 and 245° C. Its composition is given below:

Analysis:

Substance	3.242 mg.	CO ₂ — 10.209 mg.	H ₂ O — 4.109
	5.211 mg.	CO ₂ — 16.397 mg.	H ₂ O — 6.628
Composition	Carbon	Hydrogen	
	85.88 per cent	14.18 per cent	
	85.82 per cent	14.23 per cent	
For C ₇ H ₂₄ by calculation.....	85.60	14.40	

The above analysis shows conclusively that the unsulfonated hydrocarbons having the boiling range of 165-245° C contained in hydrogenated depolymerized rubber are exclusively derivatives of cyclopentane, which, as was to be expected, remained unaffected during the process of dehydrogenation.

II. HYDRODEPOLYMERIZATION OF SYNTHETIC BUTADIENE-RUBBER²

The procedure adopted was the same as that for natural rubber. The temperature was 400° C, and the hydrogen pressure was maintained at 150 atmospheres. The catalysts were molybdenum sulfide for one series and nickel deposited on aluminum oxide for the other series. The yield was 98 per cent by weight, based on the weight of the charge introduced into the reaction chamber. In the presence of molybdenum sulfide, 2.06 per cent of hydrogen took part in the reaction. In the presence of nickel as catalyst, 2.68 per cent hydrogen was used up. The gaseous products were: CO₂, less than 0.1 per cent; CO, 0.05 to 0.1 per cent; saturated hydrocarbons, 3.0 to 3.75 per cent. The liquid hydrodepolymerization product showed unsaturated properties. Its refractive index n_D^{16} was 1.5010.

Two hundred and ten cc. of the hydrodepolymerized synthetic product was divided into the following fractions by distillation:

1st fraction.....	50-100° C	14 cc.	$n_D^{18} = 1.4125$
2nd fraction.....	100-150° C	40 cc.	$n_D^{18} = 1.4410$
3rd fraction.....	150-200° C	31 cc.	$n_D^{18} = 1.4740$
4th fraction.....	up to 240° C (20 mm.)	90 cc.	$n_D^{18} = 1.5130$
5th fraction.....	residue in flask	35 cc.

These refractive indices indicate that the fractions contain appreciable quantities of saturated and unsaturated derivatives of cyclohexane, together with free aromatic compounds. This was later proved to be correct.

HYDROGENATION OF FRACTIONS

The first two fractions, when combined, yielded a mixture having a refractive index n_D^{17} of 1.4340. After reduction over platinized carbon at 160° C, this dropped to 1.4249.

The third fraction, reduced at 190° C over the same catalyst, had a refractive index n_D of 1.4590.

The fourth fraction, hydrogenated at 210° C, had a refractive index n_D^{19} of 1.4953. Treatment with concentrated sulfuric acid did not lower the refractive index (1.4935) appreciably; this indicated the almost complete absence of any unsaturated compounds after hydrogenation.

DEHYDROGENATION OF HYDROGENATED DEPOLYMERIZED SYNTHETIC RUBBER

The hydrogenation yields of the combined first and second fractions of the depolymerized rubber ($n_D^{19} = 1.4249$) were dehydrogenated over platinized carbon at 300° C. The refractive index n_D^{22} rose to 1.4418. Sulfonation with monohydrate showed that the catalytic product contained 42 per cent of aromatic substances.

The third fraction of the hydrogenated depolymer ($n_D^{19} = 1.4590$), after dehydrogenation under the conditions mentioned, had a refractive index n_D^{22} of 1.4800. By means of sulfonation, 58 per cent of aromatic compounds were obtained.

The fourth fraction of the same dehydrogenated depolymer ($n_D^{19} = 1.4953$) gave, after dehydrogenation at 325° C, a product having a refractive index n_D^{24} of 1.5090. By means of sulfonation with monohydrate, 62 per cent of aromatic compounds were found to be present.

When the total mass of depolymerized synthetic rubber was extracted by means of steam distillation to remove the most easily volatile portion, this portion could then be distilled completely in the presence of sodium between 45 and 145° C, and had a refractive index n_D^{23} of 1.4200. It exhibited a clearly unsaturated character and, when subjected to prolonged boiling (several hours) in the presence of sodium, a small portion condensed to a sticky substance, the residual hydrocarbons, however, remained unaffected. The hydrocarbons retained the same boiling point and the same refractive index (1.4200). After reduction over platinized carbon at the usual temperature, a charge of 6.190 grams absorbed 732.8 cc. of hydrogen (an indication of a considerable propor-

tion of unsaturated hydrocarbons), and yielded a totally saturated product having a refractive index n_D^{22} of 1.4120, which did not decolorize permanganate.

Analysis:

Substance	6.05 mg. 7.31 mg.	CO ₂ — 19.00 mg. CO ₂ — 22.95 mg.	H ₂ O — 7.85 mg. H ₂ O — 9.42 mg.
Composition found	Carbon	Hydrogen	
	85.65 per cent	14.51 per cent	
	85.62 per cent	14.41 per cent	
For C ₈ H ₂₀ , calculated.....	85.60 per cent	14.40 per cent	

It becomes evident that the highly volatile portion (45-145° C) of the hydrodepolymerized material consisted of hydrocarbons which, after complete reduction, yielded only cyclic compounds. This means in turn that, before reduction, the 45-145° C fraction consisted exclusively of saturated and unsaturated hydrocarbons of cyclic structure.

HYDRODEPOLYMERIZATION OF A SAMPLE OF NATURAL SMOKED SHEET

Starting with 178.8 grams of rubber, a yield of 168.4 grams of hydrodepolymerized product was obtained under operating conditions identical to those of the preceding experiment. A weight of 121.6 grams of the product was steam-distilled; 49.2 grams (40.5 per cent) passed over with the steam in the form of volatile oils, of density d_4^{20} 0.7555. These were distilled over completely in the presence of sodium within a temperature range of 48-200° C. The refractive index n_D^{20} was 1.4530. To remove the unsaturated hydrocarbons, the whole fraction was treated with 87 per cent sulfuric acid. After washing and drying, 46 grams of hydrocarbons remained. This was boiled with sodium for 2 hours without any change. With the exception of a small residue, the entire quantity was distilled between 95 and 200° C (n_D^{22} = 1.4508) and had a strong aromatic odor. This treatment with 87 per cent sulfuric acid changed the refractive index to only a slight extent. This proves that the unsaturated hydrocarbons removed from the volatile oil were cyclic and not aliphatic compounds. The residual hydrocarbons did not reduce permanganate and were, therefore, totally saturated. Sulfonation with Katwinkler reagent proved the presence of 38 per cent of aromatic compounds. The remainder was washed, dried, and distilled over sodium between 93 and 200° C ($n = 1.4310$).

Analysis:

Substance	7.83 mg. 9.51 mg.	CO ₂ — 24.64 mg. CO ₂ — 29.91 mg.	H ₂ O — 10.10 mg. H ₂ O — 12.28 mg.
Composition found	Carbon	Hydrogen	
	85.82 per cent	14.43 per cent	
	85.77 per cent	14.45 per cent	
For C ₈ H ₂₀ , calculated.....	85.60 per cent	14.40 per cent	

Thus the saturated hydrocarbons of nonaromatic nature contained in hydrodepolymerized natural rubber, and boiling within the range of 93-200° C, consist exclusively of cyclic compounds. The above experiment shows also that the fraction of the depolymerized rubber boiling between 48 and 200° C consists to a large extent (38 per cent) of free aromatic hydrocarbons.

The presence of free aromatic compounds in the hydrodepolymerization product of rubber was demonstrated likewise by the following experiment:

A sample of 41.5 grams of the hydrocarbon, which was removed easily by steam distillation, was distilled in the presence of sodium between 45 and 190° C. The distillate was clearly unsaturated, and was subjected to catalytic hydrogenation at 180° C, in the presence of platinized carbon. A single passage over the catalyst in the presence of hydrogen resulted in a catalytic product which no longer reacted with permanganate, and had a refractive index n_D^{22} of 1.4279. To determine whether all compounds had been completely reduced, the product was treated with Katwinkels mixture, and 12 per cent of aromatic compounds were found to be present. The remaining unsulfonated portion was washed, dried, and distilled in the presence of sodium. The major portion distilled between 130 and 160° C, and its refractive index n_D^{21} was 1.4297.

Analysis:

Substance	4.341 mg.	CO ₂ — 13.642 mg.	H ₂ O — 5.615 mg.
	5.158 mg.	CO ₂ — 16.190 mg.	H ₂ O — 6.662 mg.
Composition found	Carbon	Hydrogen	
	85.71 per cent	14.47 per cent	
	85.61 per cent	14.45 per cent	
For C _n H _{2n} calculated.....	85.60 per cent	14.40 per cent	

Thus, this experiment confirms the presence of free aromatic compounds in the reduction product of hydrodepolymerized rubber. A single reducing operation was insufficient to effect complete hydrogenation of the aromatic compounds, and a portion of these remained unchanged.

Once again the hydrocarbons remaining after sulfonation proved to be cyclic compounds in all probability largely composed of derivatives of cyclopentane.

III. CONCLUSIONS

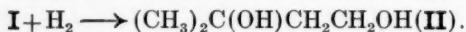
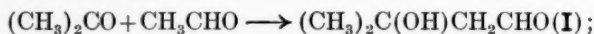
The results of the present investigation compel us to view the structure and chemical nature of rubber in a somewhat different light. Apparently rubber is actually a polyterpene, (C₅H₈)_x, consisting of associated molecules of unsaturated cyclic hydrocarbons, derivatives of cyclohexane and cyclopentane, for instance, vinylcyclohexane. That this is so may be seen from the well known fact that carbonization (dry distillation) of rubber yields considerable dipentene, and the product of its depolymerization, isoprene. Rubber, both natural and synthetic, is a polyterpene in which molecules of isoprene and also of butadiene, converted into their respective cyclic dimers, are combined with each other, forming long chains, every link of which is a closed system of atoms.

The present-day concept of the structure and chemical nature of rubber is based largely on the study of the viscosity of solutions of rubber in various solvents (Staudinger and his school), and based only in part on the study of x-ray diagrams of rubber. The conclusions reached are that rubber consists of a large number of isoprene or butadiene molecules held together in a labile way, in the form of long threadlike chains of unsaturated and paraffinic nature.

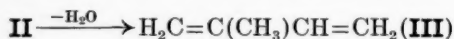
The authors of this paper hold the view that the aromatic hydrocarbons found in the product of the hydrodepolymerization of rubber, and present in a free state, were formed under the conditions of the experiments, and are closely related to the structure of the original rubber. They were formed as the result of irreversible catalysis of the unsaturated derivatives of cyclohexene, which are the first and immediate products of the diene synthesis from both butadiene and isoprene. It should be remembered that, under the influence of contact catalysis, vinylcyclohexene is converted into ethylbenzene and diethylcyclohexane³.

It is difficult to imagine that such considerable quantities of hydrocarbons of the cyclohexene and of the aromatic types as are found among the depolymerization products of rubber could have arisen from threadlike chains of paraffinic structure, the links of which are built up of aggregates of isoprene or butadiene molecules. The depolymerization of rubber was carried out at an elevated pressure of hydrogen and at a temperature of 400° C, the latter being too low for the formation of aromatic compounds. Thus the conditions were distinctly unfavorable for the formation of aromatic hydrocarbons from a rubber which, according to present-day concepts, is a complex association of molecules of unsaturated aliphatic hydrocarbons bound together to form a threadlike structure.

The question arises as to the method by which the plant organism produces rubber under natural conditions. To date, the most likely hypothesis is that due to Aschan. According to this hypothesis, rubber is formed by a series of chemical changes from acetone and acetaldehyde. These compounds can readily be formed by decomposition of carbohydrates, so abundantly present in the cell-sap and in the tissues of plants. If we assume the temporary appearance of acetone and acetaldehyde in plants due to a fermentation process, then the synthesis of isoprene from the above comparatively simple primary materials can be visualized as follows:



The methylaldol (I), formed is, when subjected to reduction, converted into 1,1-dimethyltrimethyleneglycol (II), which splits off water, with formation of isoprene (III):



Isoprene in turn is that paraffinic hydrocarbon, with double bonds, from the molecules of which rubber is made up, rubber being a highly polymerized product of isoprene.

Yet it is in no way possible to determine the presence of any isoprene in the free state in the milky sap of the rubber plant. Even in the sap, it is present in a highly polymerized state.

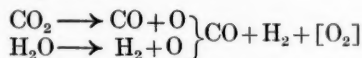
In addition to rubber hydrocarbon, predominantly present, the milky sap of the plant contains limited quantities of sugars, ferments, albumins, resins, ethereal oils, organic acids, and mineral salts. All these substances, occurring with rubber, are formed by synthetic reactions in the plant, and are present in the milky sap merely as mechanical admixtures. Neither acetone nor acetaldehyde has ever been found among them. It is altogether doubtful that Aschan's hypothesis explains the mechanism of the natural synthesis of isoprene by the plant.

The catalytic hydrogenation of carbon monoxide leads to the synthesis of fuel oil (F. Fischer and collaborators), consisting of a whole series of paraffinic hydrocarbons. It seems conceivable (N. D. Zelinsky), that the primary source for the synthesis of isoprene by the plant is again carbon monoxide, and that isoprene is a product of assimilation of carbon dioxide under the influence of light and chlorophyll, like starches or carbohydrates in general.

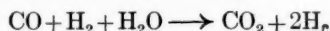
Chemically, carbohydrates and hydrocarbons are vastly different substances, but this should not exclude the possibility of their simultaneous occurrence by the action of ferments and enzymes as a result of oxidation-reduction processes to which the carbon monoxide (the first immediate product of the assimilation

of carbon dioxide) is subjected. This picture of the plant synthesis of isoprene does not contradict in any way the interesting observation, made by plant physiologists⁴, that when *Ficus elastica*, for instance, is raised in an atmosphere and in soil devoid of carbon dioxide, the milky sap becomes gradually poorer in rubber and, after a period of time, becomes pure water. Similarly important is the observation that the milky sap of the *Chondrilla ambigua* Fisch plant undergoes a reduction in rubber content⁵ when this plant is left without sunshine. This leads to the conclusion that the formation of rubber takes place simultaneously with the assimilation of carbon dioxide.

The synthesis of isoprene in the plant can be visualized as following the mechanism of the process of assimilation:



The "water gas" ($\text{CO} + \text{H}_2$) formed in the nascent state leads in one case to the formation of methylene oxide, CH_2O , which further condenses to form the carbohydrate, $(\text{CH}_2\text{O})_6$. In the other case, the carbon monoxide is converted under the influence of water into CO_2 and H_2 :

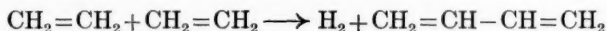


The hydrogen formed in the course of this reaction hydrogenates the carbon monoxide into a free radical of methylene:

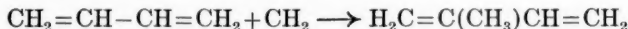


The methylene radical is the starting point for the formation of ethylene, $\text{CH}_2=\text{CH}_2$, both under laboratory conditions and in nature.

By catalytic dehydrogenation, ethylene can be converted into butadiene:

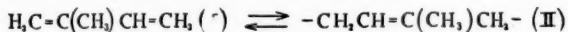


which, entering into reaction with a methylene radical, yields methylbutadiene, *i.e.*, isoprene:

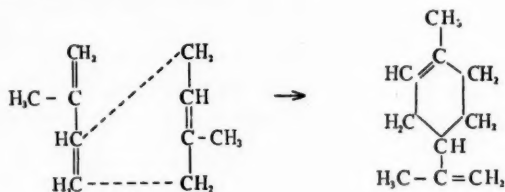


It must be assumed that the synthesis of isoprene in the cells and tissues of the plant organism, endowed with the necessary catalysts, proceeds by simple processes, such as the reactions outlined above.

By the mechanism of diene synthesis, isoprene apparently forms its dimer, dipentene. The molecule of isoprene can exist in two isomeric forms in equilibrium.



Form (II), having free valences at its end carbon atoms, forms dipentene (1-methyl-4-propenylcyclohexene-6):



Thus, isoprene easily polymerizes to the ring-shaped system of dipentene, which in turn is capable of further condensation, either with other dipentene molecules or with isoprene itself. Thus, condensed cyclic polymers of isoprene are formed. Interassociated polymerization products of isoprene form rubber. This explains why the hydrodepolymerization of rubber yields such a large proportion of aromatic compounds, as we have shown in our experiments.

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- ² Refined synthetic rubber of high plasticity.
- ³ *Proceedings of the Organic Chemistry Conference of the Academy of Sciences of the U. S. S. R. M.*, **1939**, page 10.
- ⁴ Spence, *Lecture on India Rubber*, **8**, 141 (1908).
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THE MOLECULAR WEIGHTS OF RUBBER AND RELATED MATERIALS

I. EXPERIMENTAL METHODS *

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The molecular weight of a high polymeric material may be measured by three types of method, involving (1) use of an ultracentrifuge, (2) measurement of the osmotic pressure of a solution or some thermodynamically related quantity, and (3) application of Staudinger's well known equation to calculate the molecular weight from the viscosity of a dilute solution. The difficulty and expense of erecting an ultracentrifuge precludes its general use, and our attention has been confined to the two remaining methods. In this paper we describe the various forms of apparatus employed, and discuss the interpretation of the experimental results. Application of these methods is considered in papers to follow.

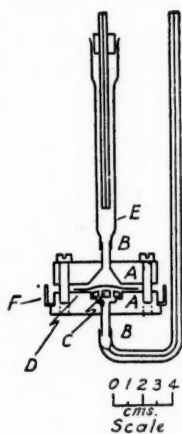


FIG. 1.—Construction of osmometer.

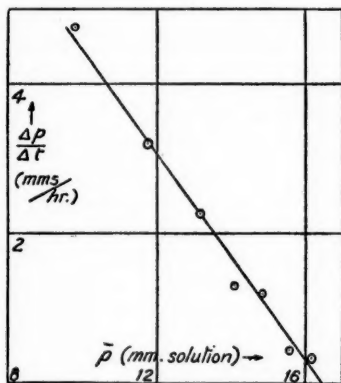


FIG. 2.—Osmotic pressure of gel rubber in benzene + 15% MeOH at 25° C.

(1) OSMOTIC METHODS

(a) A NEW FORM OF OSMOMETER

Various forms of osmometer have been described¹; the one employed in this work is shown in Figure 1. The cells which contain the solvent and solution are turned out of two substantial brass cylinders A, and are connected to glass tubes by means of copper-glass seals B, which are soldered into the brass blocks. These seals are tested before use, and rejected unless vacuum-tight. The lower cell

* Reprinted from the *Transactions of the Faraday Society*, Vol. 36, Part 11, pages 1162-1178, November 1940.

communicates with a fine capillary tube (approximately 0.5 mm. diameter), which is bent into a U-shape as shown. The volume of this cell must be kept as small as possible to minimize the fluctuations of the liquid level in the capillary consequent on temperature variations. Most of the volume of the cell is, therefore, filled by a perforated brass plate C, the upper surface of which is slightly domed and covered by a piece of fine copper gauze, soldered round the edges; the object of this plate is to support the membrane D. The upper cell terminates in a glass tube E, of bore approximately 2 mm. greater than the external diameter of the capillary tube inserted in it. This capillary is of the same bore as that attached to the lower cell, to permit direct reading of the pressure head across the cell without a capillarity correction. The hydrostatic pressure can be adjusted by moving the capillary up or down in the tube E. The inner faces of the brass cylinders are carefully polished flat and the two cells firmly clamped together by a ring of eight o BA screws: no trouble has ever been experienced from leakage between these faces. The outer ring F fits tightly around the lower cell, and enables the face of this cell to be completely flooded with solvent when assembling the osmometer. The membranes used were obtained from Membranfilter-Ges. m.b. H., Göttingen, and are the grade known as "ultracellafilter, feinst." They were obtained wet with water and, before use, are washed with alcohol and then with the solvent to be employed. The cells are cleaned by steaming and then washing with acetone, followed by the solvent to be used. Plate C is heated in a little boiling solvent to expel air entrapped by the gauze. In filling the osmometer, the lower cell is flooded with solvent, any air bubbles removed from the capillary, and the plate and membrane placed successively in position. The upper cell is then lowered into place and clamped down before the whole assembly is suspended by a suitable cradle in a water thermostat. The upper cell is filled and emptied by means of a tube, whose length is adjusted so that its tip just touches the membrane. In changing from one solution to another, it is sufficient to suck out the old solution, wash with two changes of the new solution, and fill. Washing is carried out by sucking the solution up into the filling tube and allowing it to flow back again: this is usually repeated three times. The advantage of this arrangement is that it is unnecessary to dismantle the osmometer to change solutions. If the membrane were perfectly semi-permeable, the solvent in the lower cell would remain unchanged indefinitely. In practice the upper cell is filled with solvent after each osmotic pressure measurement to check the constancy of the zero, and a correction is applied for the small pressures which are found. If the solution admitted to the upper cell contains a diffusible component, some of this will find its way into the lower cell, from which it can only be removed again, either by dismantling the osmometer or by prolonged washing of the upper cell with repeated changes of solvent: the latter is usually the simpler method. In this way the life of an osmometer, once assembled, is very long.

Two methods are available for estimating the equilibrium osmotic pressure: (1) the static method, in which osmosis is allowed to continue until equilibrium is attained, and (2) the dynamic method, in which the rate of osmosis is measured as a function of the pressure head across the osmometer and the osmotic pressure obtained by interpolating to zero rate of osmosis. Both these methods are readily applied to the present osmometer. If the pressure head p is observed as a function of time t , the rate of osmosis is measured by dp/dt , and an extrapolation of the linear plot of $dp/dt - p$ enables the osmotic pressure to be estimated within about 5-8 hours of introducing the solution. If the solution is

allowed to remain in the osmometer overnight, an equilibrium value is also obtained, which in general agrees well with the dynamic value. Experience leads us to prefer the dynamic value when a discrepancy is found, since this can generally be attributed to instability of the solution, to very slow diffusion of solute through the membrane, or to slight contamination of the solution. Whichever method is employed, accurate temperature control is essential, but this is doubly necessary with the dynamic method to prevent apparent rates of osmosis being complicated by thermal oscillation of the level in the lower cell. The thermostat employed in the present work is heated by a radiator lamp and controlled by a large spiral mercury-toluene thermoregulator and Sunvic relay. By careful arrangement of the stirrer, heater and regulator the temperature fluctuation at 25° C has been reduced to $\pm 0.003^\circ$ C without any lagging.

The results of a typical experiment are set out in detail below:

TABLE I

OSMOTIC PRESSURE OF GEL RUBBER IN BENZENE + 15% METHANOL.
CONCENTRATION OF SOLUTION = 1.21 GRAMS PER 100 CC. SOLUTION.
OSMOMETER FILLED 0930 HR.

Time	Osmotic pressure p (mm. solution)	$\Delta p / \Delta t$ (mm. solution) (hrs.)	\bar{p} (mm. solution)
1003.....	8.6 ₂	—	—
1032.....	10.9 ₂	4.7 ₅	9.7 ₇
1104.....	12.6 ₁	3.2	11.7 ₇
1134.....	13.7 ₄	2.2 ₅	13.1 ₇
1205.....	14.4 ₀	1.3	14.0 ₇
1249.....	15.3 ₀	1.2	14.8 ₅
1405.....	15.8 ₅	0.4 ₅	15.5 ₇
1552.....	16.4 ₀	0.3 ₅	16.1 ₅

$\Delta p / \Delta t$ represents the mean rate of osmosis over the interval between two successive pressure readings; p is the mean of these two pressures. A plot of $\Delta p / \Delta t$ against \bar{p} is given in Figure 2, and extrapolation to zero rate of osmosis gives for the osmotic pressure a value of 16.4 mm. of solution. This is to be compared with the static value (after standing overnight) of 16.8 mm. As already explained, the former value is taken to be correct. The normal experimental error is estimated to be not more than ± 0.5 mm.

(b) THE METHOD OF ISOTHERMAL DISTILLATION

The vapor pressure lowering produced by dissolving a high molecular substance is difficult to measure directly, but it can be obtained by measuring the rate at which the solvent distills isothermally into the solution. The apparatus used is shown in Figure 3, and is essentially the same as one described by Signer². It consists of two bulbs, of 3-4 cm. diameter, connected by a short wide bridge. Side tubes, subsequently sealed off, are provided for filling and evacuating. Perpendicular to the plane of the bridge and side tubes, a measuring tube of approximately 4 mm. bore is sealed onto each bulb, its lower end being expanded into an elongated bulb of 3-4 cc. volume. A reference mark is provided on each measuring tube, and the volumes of liquid in the bulbs adjusted so that both levels are in the measuring tubes. The method of working is as follows: solvent and solution are pipetted into the two bulbs, which are then turned into position (b), and the measuring tubes are cooled in liquid air.

One side tube is sealed off, the other constricted, and sealed on to the vacuum line. The apparatus is then thoroughly outgassed by successive pumping, melting and freezing: three pumpings suffice, after which the second side tube is sealed off *in vacuo*, and the apparatus is mounted in a suitable clamp and placed in the thermostat. The principal error in reading the liquid levels arises from drainage, and it is therefore necessary to standardize the conditions. The apparatus is allowed to warm up in position (a), then turned to (b) and 0.5 hour is allowed before the levels are read by means of a cathetometer. The apparatus is then returned to position (a) for a measured length of time while distillation occurs, after which 0.5 hour is again allowed in position (b) before reading the new levels.

Signer's method of obtaining molecular weights was to employ, instead of pure solvent, a solution of known vapor pressure, and to allow distillation to occur until equilibrium was established. This was a very laborious procedure, even though accelerated by periodical thermal distillations in the direction indicated by the isothermal distillation. It was, therefore, thought desirable to

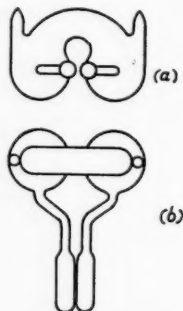


FIG. 3.—Isothermal distillation apparatus.

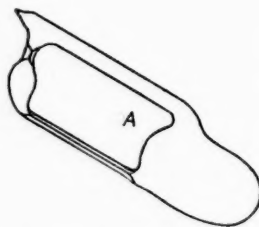


FIG. 4.—Vacuum viscometer.

attempt to base calculations on the rate of distillation of pure solvent into the solution, and calibration experiments were carried out, using solutions of known vapor pressure. These showed that the rate of distillation was proportional to the vapor pressure difference between the two bulbs: the following figures represent a typical calibration. The solute employed was olive oil, which for present purposes may be taken to be triolein. If p is the vapor pressure of the solvent (benzene) and Δp the vapor pressure lowering produced by the solute, $\Delta p/p$ is calculated from the mole fraction of olive oil in the solution. If R is the observed rate of distillation (mm. of measuring tube per hr.) the results are expressed in terms of a constant k , given by:

$$\frac{\Delta p}{p} = k \cdot R$$

The linear relation between $\Delta p/p$ and R is seen from these figures to hold down to $\Delta p/p = 10^{-4}$, i.e., an actual difference of vapor pressure of approximately 0.01 mm. This represents the lowest value which can be measured with any accuracy; for a 1 per cent solution, this is equivalent to a molecular weight of approximately 10,000 and since, as will be shown below, measurements in concentrated solutions are difficult to interpret, 10,000 to 20,000 represents the

upper limit of molecular weights measurable by this method. Probably the limiting factor is the accuracy of temperature control which can be achieved. If the two bulbs are both filled with benzene at 25° C, and there is a small temperature difference ΔT (°C.) between them, the vapor pressure difference is given (from the known $p \sim T$ curve of benzene) by:

$$\Delta p/p = 0.046 \Delta T$$

Thus, a vapor pressure difference of $\Delta p/p = 10^{-4}$ is equivalent to $\Delta T = 0.0022^\circ \text{C}$ and, to measure the isothermal distillation corresponding to this vapor pressure lowering, it is essential that any consistent temperature difference between the two bulbs shall be small compared with 0.0022°C . The regular fluctuation of the 25°C thermostat employed does not exceed $\pm 0.003^\circ \text{C}$ and, in an attempt to minimize the effect of temperature gradients, the apparatus was in later experiments, rotated during the distillation. The reproducibility attained in the

TABLE II
CALIBRATION OF ISOTHERMAL DISTILLATION BULBS FOR BENZENE
SOLUTIONS AT 25°C

Concentration of solution, g. olive oil	$\Delta p/p$ (calculate)	R (mm. per hr.)	k (hr. per mm.)
100 cc. solution			
1.00.....	1.02×10^{-3}	0.275	3.7×10^{-3}
0.300.....	3.04×10^{-4}	0.074	4.1×10^{-3}
0.100.....	1.01×10^{-4}	0.027	3.7×10^{-3}
Mean			3.8×10^{-3}

measurement of a fairly high molecular weight is indicated by two figures for a rubber degradation product:

Apparatus	k	Rate of distillation mm. per hr.	$\Delta p/p$	Molecular weight
E	3.8×10^{-3}	0.037	1.4×10^{-4}	6,700
J	2.3×10^{-3}	0.055	1.5×10^{-4}	6,100

Although very much faster than Signer's method, the procedure is still somewhat slow, and it was thought possible that the rate-controlling factor was the attainment of equilibrium between the bulk and surface of the liquid. A new form of apparatus was therefore designed, in which the liquid could be shaken during distillation, but the rate of distillation was smaller than usual, due no doubt to the use of a narrower bridge tube. The rate-controlling factor is therefore the diffusion of the vapor, and all that can be done to accelerate distillation is to make the bridge as short and wide as possible. The distillation is not very sensitive to traces of air; introduction of air to a pressure of 6.2 mm. reduced the rate by approximately 50 per cent.

The method is not likely to find very general application, but it has a number of important advantages for special purposes. Thus it can be used with materials which are unstable in air, since all measurements are conducted *in vacuo*. Further, it is applicable to any temperature between the freezing and boiling point of the solvent. For molecular weights between 1,000 and 20,000, it is more accurate than a cryoscopic or ebullioscopic measurement, but for higher molecular weights it must be replaced by direct observation of the osmotic pressure.

(2) THE VISCOSITY METHOD

The basis of the viscosity method is the use of the Staudinger equation³, according to which the specific viscosities of dilute solutions of a homologous series of linear polymers are proportional to their molecular weights and to their concentrations:

$$\eta_{sp} = K_m c M$$

In practice, η_{sp}/c is found to be a function of c and it is, therefore, necessary to measure η_{sp} at several concentrations, extrapolate to infinite dilution⁴, and write:

$$M = K \lim_{c \rightarrow 0} (\eta_{sp}/c)$$

To be able to carry out this extrapolation with precision, measurements must be made of specific viscosities as low as 0.05, so the viscosities of the solvent and solution must be known with a high relative accuracy. This accuracy is difficult to attain with a rotating cylinder viscometer, and a capillary flow type of instrument, has, therefore, been employed, despite its theoretical disadvantages (referred to below).

The viscometers were constructed in Pyrex, from a design based on that described by Washburn⁵, but were much smaller, the approximate dimensions of a typical model being as follows: Volume of small bulb between reference marks 2 cc., diameter of liquid surface in large bulb 4 cm., length of capillary 33 cm., radius of capillary 0.35 mm., mean head of liquid during flow 9 cm., total volume of liquid required 8 cc., flow time for benzene at 25° C, 80 seconds.

To measure a specific viscosity of 0.05, correct to 1 per cent, requires each individual viscosity to be accurate to 0.025 per cent. Variations of 0.025 per cent would be produced by any of the following errors:

(1) The change in hydrostatic pressure arising from an error in the volume of liquid used of 0.03 cc.; the pipetting error should not exceed this figure.

(2) A temperature variation of 0.01° C; the thermostat fluctuation does not exceed $\pm 0.003^\circ$ C.

(3) An error of 1.3° in levelling the viscometer. The viscometer is rigidly clamped to a brass rod whose upper end carries a horizontal plate fitted with levelling screws: these are adjusted to level the horizontal plate in two directions at right angles. The viscometer is not removed from the clamp for cleaning, so the levelling is quite reproducible.

(4) An error of 0.02 second in timing the flow. The flow is timed by a stop watch making 30 beats per second, and is easily read to 0.03 second.

A series of 4 or 5 measurements is made, and the maximum deviation is usually less than 0.1 second, with a mean deviation from the average of not more than 0.03 second.

The overall relative error in the measurement of a viscosity is estimated to be less than ± 0.1 per cent, molecular weights can consequently be measured with an accuracy of ± 5 per cent. In practice this figure is probably improved; the reproducibility of results suggests that an accuracy of ± 2 per cent is usually attained.

It has on occasion been necessary to measure viscosities *in vacuo* and, for this purpose, a viscometer was constructed, as shown in Figure 4. The solution is poured into the large bulb through the side tube, which is then sealed on to the vacuum line. After outgassing the solution, the side tube is sealed off, and the

viscometer mounted in a clamp pivoted about the point A so that the solution can be run from one bulb to the other by tilting the viscometer suitably. It is, of course, necessary to ensure that the viscometer is always in the same position for measurement: this is accomplished by supporting the pivot from a plate equipped with levelling screws, and adjusting the clamp by means of an extension rod fitting into a slot cut out of the plate. The large horizontal displacement of the two bulbs precludes high accuracy, but this was not needed in this particular work.

INTERPRETATION OF RESULTS

(a) OSMOTIC DATA

Interpretation of the osmotic pressure or vapor-pressure lowering of solutions of high molecular weight compounds is complicated by the fact that such solutions do not in general show ideal behavior, *i.e.*, the osmotic pressure is not proportional to the concentration, but increases considerably more rapidly. If Π is the osmotic pressure and c the concentration, the ideal van't Hoff law has the form $\Pi/c = RT/M$, where M is the molecular weight. To eliminate the variation of Π/c with c , it is necessary to extrapolate to infinite dilution, and write:

$$M = RT / \lim_{c \rightarrow 0} (\Pi/c)$$

The departure from ideal behavior is generally ascribed to solvation, the dissolved particles carrying with them so much solvent that their effective concentration is reduced. Provided they are individually solvated, extrapolation to infinite dilution eliminates this error. Even if association of the particles occurs, measurements in sufficiently dilute solution would be expected to permit an extrapolation to the unassociated state at infinite dilution. The extent of the variation of Π/c with c depends on both the solvent and the solute, and all data hitherto published for rubber solutions show particularly large deviations. It is, therefore, important to have some knowledge of the law relating Π/c to c , and a number of equations have been suggested. Sackur⁶ assumed the volume of solvent removed by solvation to be independent of the solute concentration; his equation may be put in the form:

$$\Pi(1/c - b) = RT/M$$

or

$$\Pi/c = RT/M + b\Pi$$

Thus Π/c should be a linear function of Π . Meyer and Mark⁷ have employed this method to extrapolate their data for crepe solutions. Ostwald⁸ suggests that the deviation is to be ascribed to a swelling pressure, and he adds an empirical correcting term:

$$\Pi = \frac{c}{M} \cdot RT + kc^n$$

The second term has the same form as the expression for the swelling pressure of rubber in a number of solvents, found empirically by Posnjak⁹, who obtained values of n lying between 2.48 and 3.33. Carter and Record¹⁰ find Ostwald's equation to hold over a wide range of concentrations for a large number of polysaccharide solutions, with values of n a little more than 2. Meyer Wolff and

Boissonas¹¹ show that, for solutions of masticated rubber in toluene, the equation holds accurately with $n=2$, so that Π/c is a linear function of c .

Schulz¹² has modified Sackur's equation by assuming that b can be represented as a function of Π by an equation analogous to Posnjak's equation for the swelling pressure. Putting $\Pi = kb^{-n}$ and eliminating b he obtains:

$$M = \frac{RTc}{(1 - c^n \sqrt{k/\Pi})}$$

where n should have values of the order of those found by Posnjak. For the purposes of extrapolation this may be more conveniently transformed to:

$$\Pi/c = RT/M + Kc^\alpha, \text{ where } K = k^{1/n}, \alpha = 1 - 1/n \approx 0.5$$

Hence a plot of Π/c against $\sqrt{\Pi}$ should be nearly linear. There are, thus, three ways of extrapolating Π/c to infinite dilution, all of which have been claimed to give nearly linear plots:

- (1) $\Pi/c \sim \Pi$; (2) $\Pi/c \sim c$; (3) $\Pi/c \sim \sqrt{\Pi}$

In Figure 5, the data of Meyer, Wolff and Boissonas have been extrapolated by these three methods, and it is at once evident that (1) can be eliminated.

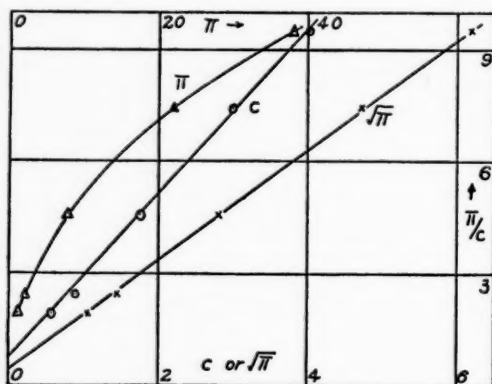


FIG. 5.—Osmotic pressure of milled crepe in toluene.

Either of the other plots is linear within experimental error, but they extrapolate to give very different molecular weights, viz., from (2) 270,000; from (3) 490,000. Careful consideration of the data shows that these two curves cannot be distinguished experimentally, as the difference occurs almost entirely at very low concentrations, Schulz's equation requiring the $\Pi/c \sim c$ curve to dip sharply downwards for very low concentrations. Schulz claims to have shown this behavior experimentally for polystyrene solutions, but the evidence is not very convincing. It is to be noted also that his equation requires the solvation to become infinite at infinite dilution, which cannot be true. Furthermore, employing a solvent in which rubber forms solutions which are much more nearly ideal than in toluene, our experimental evidence (Part II) supports Ostwald's form of equation, and this is, therefore, taken to be correct.

(b) VISCOSITY DATA

Staudinger's viscosity equation has been very widely used, but its application requires much greater care than has usually been exercised. There are two separate points to be discussed: (1) the measurement of specific viscosity, and (2) the relationship between viscosity and molecular weight.

Measurement of the specific viscosity of high-molecular substances is complicated by the fact that such solutions show anomalous viscosity, the viscosity becoming lower as the rate of shear is increased. The effect can be eliminated by measuring the viscosity at low rates of shear and extrapolating to zero rate of shear, as has been done by Robinson¹³. In a capillary viscometer, the rate of shear is high, and varies across the tube, but it has been shown¹⁴ that the specific viscosities of a series of polyvinyl acetates, measured by a capillary viscometer, were closely proportional to the corresponding values found with a Couette viscometer at a rate of shear of 1.9 radians per second. Furthermore, if the specific viscosity of a dilute solution is measured in a series of similar—but not identical—capillary viscometers, the same result is obtained in each. The specific viscosity does, however, depend on the solvent employed, a fact which is undoubtedly related to the varying solvation which occurs in different solvents.

The relationship between viscosity and molecular weight has been the subject of a number of theoretical investigations of which the most complete is that of Huggins¹⁵. His conclusion is that, for dilute solutions of sufficiently long linear molecules, the Staudinger law should hold. At present the equation can only be satisfactorily based on experiment, and must be tested for each class of material to which it is to be applied.

Comparison of viscosity and osmotic data is only strictly valid for homogeneous materials, since the viscosity of a mixture depends on the weight average molecular weight¹⁶, while the osmotic pressure measures the number average. These two averages may be defined thus¹⁷:

$$\text{Number average molecular weight} = M_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$\text{Weight average molecular weight} = M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

where n_i is the number of molecules of weight M_i and the summations are over all values of i . The ratio M_w/M_n increases with increasing heterogeneity of the mixture.

The general conclusion, based on our own experiments, supplemented by the most reliable published data, is that the intrinsic viscosity is, to a good degree of approximation, a measure of the molecular weight of a material known to consist of long linear chains, provided that measurements are always made in the same solvent, and are extrapolated to infinite dilution. The Staudinger law does not apply at all to spherical molecules and, in the case of molecules which are only approximately linear, *e.g.*, branched molecules, gives the length rather than the molecular weight of the material. It is clear that measurement of the intrinsic viscosity of an unknown material will not necessarily give the molecular weight: something must first be known about its structure. Alternatively, given its osmotic molecular weight and intrinsic viscosity, some tentative conclusions may be drawn regarding its structure.

SUMMARY

A new form of osmometer for use with nonaqueous solutions is described. A method of measuring the vapor pressure lowering produced by a solute from the rate of isothermal distillation of solvent into the solution has been worked out and shown to be applicable to the measurement of molecular weights up to 10,000. The calculation of molecular weights from the osmotic pressures of nonideal solutions is discussed. The basis of the viscosity method of determining molecular weights is critically examined.

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- ¹ Carter and Record, *J. Chem. Soc.* **1939**, 660; Schulz, *Z. physik. Chem. [A]*, **176**, 317 (1936); Meyer, Wolff and Boissonas, *Helv. Chim. Acta*, **23**, 430 (1940).
- ² Singer, *Ann.* **478**, 246 (1930).
- ³ Staudinger, "Die Hochmolekularen Organischen Verbindungen", Julius Springer, Berlin, 1932.
- ⁴ It is usually simpler to extrapolate the intrinsic viscosity $[\eta]$, defined as $(1/c)\log_e (1+\eta_{sp})$, rather than η_{sp}/c . These quantities are identical at infinite dilution, but whereas η_{sp}/c rises rapidly with c , $[\eta]$, which must always be less than η_{sp}/c , is often nearly independent of c . It is possible also to estimate the intrinsic viscosity at infinite dilution $[\eta]_0$ approximately from a single observation at higher concentration by making use of the empirical equation of Philippoff (RUBBER CHEM. TECH. **10**, 76 (1937)): $1+\eta_{sp}=(1+[\eta]_0 c/8)$ (cf. *Kolloid-Z.* **49**, 60 (1929)). Although this equation holds surprisingly well over a very wide range of concentrations of rubber solutions in toluene (up to 4 per cent), it is not strictly accurate even for dilute solutions, and is therefore of no assistance in extrapolating to infinite dilution.
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- ⁸ Ostwald, *Kolloid-Z.* **49**, 60 (1929).
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II. OSMOTIC PRESSURE AND VISCOSITY OF SOLUTIONS OF RAW RUBBER

Raw rubber is such a variable material that it is not possible to assign to it a definite molecular weight. The value obtained will necessarily differ from sample to sample, although experience shows that this variation is not so large as might have been expected. The absolute values reported in this paper apply therefore only to the particular samples examined, but the order of magnitude will be correct for any similar materials. The object of this paper is to report a series of precise determinations of the osmotic pressure and viscosity of raw rubber and rubber fractions in various solvents, and to consider the application of the Staudinger equation to rubber solutions.

OSMOTIC PRESSURE MEASUREMENTS

A number of attempts have been made in the past to calculate the molecular weight of raw rubber from osmotic pressure data, some of the results are given in Table I.

From the last column, it is to be noted that two different methods have been employed in extrapolating the data to infinite dilution. Now these methods cannot both be correct and, as observed in Part I, they may lead to quite different values for the molecular weight. It does not seem possible to resolve the difficulty from the published figures. Plots of $\Pi/c \sim \Pi$, which are linear if Sackur's

equation is valid, are actually found to be linear from published data. Similar plots for the remaining data of Table I are not linear, but concave downwards, and therefore cannot be extrapolated (*cf.* Figure 5 of Part I). On the other hand, the data of references (1) and (4) can be extrapolated by a linear plot of $\Pi/c \sim c$ (Ostwald's method), while attempts to extrapolate the data of references (2) and (3) in this way lead to nonlinear plots from which $(\Pi/c)_0$ cannot be accurately estimated. The trouble undoubtedly arises from two sources: (1) the difficulty of measuring accurately the osmotic pressure of dilute solutions, and (2) the wide deviation of the solutions from ideal behavior. The extent of the latter phenomenon may be seen by calculating the osmotic coefficients of the various solvents in solutions containing 1 gram of rubber per 100 cc., *i.e.*, the ratio between Π/c observed for these solutions and Π/c at infinite dilution¹. The figures given for these coefficients in Table I have been calculated from the various authors' values of $(\Pi/c)_0$ and are, therefore, subject to the same errors as those involved in the molecular weight calculation.

It is clear that extrapolation to infinite dilution would be greatly facilitated if a solvent could be found in which rubber formed more nearly ideal solutions.

TABLE I
OSMOTIC MOLECULAR WEIGHTS OF RUBBER

Material	Solvent	Temp. (° C)	Molecular weight $\times 10^{-5}$	Osmotic coefficient in 1% solution	Method of extrapolation to infinite dilution
Deresinified pale crepe ¹	Benzene	25	1.5 ₆	2.3	Ostwald
Deresinified pale crepe ²	Petrol-ether	25	1.0 ₃	1.67	Ostwald
Crepe ³	Benzene	7	3.6	1.7	Sackur
Crepe ³	Chlorobenzene ..	7	1.8 ₃	1.43	Sackur
Ether sol from crepe ⁴	Benzene	11	1.9	1.43	Sackur
Ether sol from crepe ⁴	Benzene	40	1.9	1.92	Sackur
Lightly milled crepe ⁵	Toluene	24.4	2.7	4.0	Ostwald

If we accept the view that the nonideality arises from the removal of free solvent by solvation of the dispersed rubber, the most nearly ideal solvent will be one which produces the minimum of solvation. It is, perhaps, significant in this connection that the osmotic coefficient of petrol ether was found by Caspari² to be less than that of benzene, which is known to be the more active swelling agent for rubber⁶. The search for a more ideal solvent therefore proceeded along two lines: (1) In certain homologous series, *e.g.*, the acetic esters, an increase in molecular weight is accompanied by a progressive increase in swelling power for rubber. At a fixed temperature there is a line of sharp division between the lower members, which are nonsolvents, and the higher members, which dissolve rubber completely⁷. By choosing a liquid just on the solvent side of the line, it should be possible to limit solvation to a low value. (2) Addition of a polar nonsolvent to concentrated solutions of rubber greatly reduces the viscosity, and the phenomenon has been ascribed to desolvation of the rubber particles. The use of mixtures of solvent and nonsolvent is, therefore, worth examination. The three solvents finally examined were:

(1) Amyl acetate.

(2a) Benzene-ethyl alcohol mixtures containing 100 cc. of alcohol per liter.

(2b) Benzene-methyl alcohol mixtures containing 150 cc. of alcohol per liter.

Osmotic pressures of solutions of crepe rubber were measured, as described in Part I. Precautions must be taken to prevent oxidation while the solutions

are being prepared. The weighed rubber is covered with solvent, and the tube is cooled in liquid air. After thoroughly outgassing—by successive pumping, melting and freezing—the tube is sealed *in vacuo* and shaken mechanically until the rubber dissolves. Dilution to the required concentration and subsequent measurement of the osmotic pressure is carried out in air, but solutions are stored in the dark. These precautions have proved adequate in practice, but degradation occurs if solutions are shaken in air or allowed to stand for long periods exposed to air and light.

In Figure 1, the osmotic data are plotted in the form $\Pi/c \sim c$, where Π is in mm. Hg and c in grams of rubber per 100 cc. solution. The extrapolated values $(\Pi/c)_0$, calculated molecular weight, and osmotic coefficients g of the various solvents in 1 per cent solutions are collected in Table II:

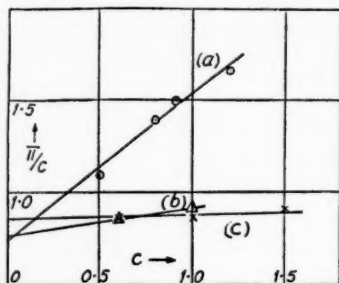


FIG. 1.—Osmotic pressure of crepe solutions at 25° C.

- (a) Benzene+10% ethanol.
- (b) Amyl acetate.
- (c) Benzene+15% methanol.

TABLE II

OSMOTIC MOLECULAR WEIGHTS OF CREPE AT 25° C

Solvent	$(\Pi/c)_0$	$M \times 10^{-5}$	g (1%)
Amyl acetate	0.76 ± 0.05	2.4 ± 0.2	1.17
Benzene + 10% ethanol	0.73 ± 0.10	2.5 ± 0.3	2.1
Benzene + 15% methanol	0.85 ± 0.03	2.2 ± 0.1	1.02

It is at once evident that the last solvent gives solutions which are so nearly ideal that the necessity for extrapolation to infinite dilution is largely removed, the molecular weight being directly calculable from the osmotic pressures of solution containing 1 to 1.5 grams of rubber per 100 cc. solution. The osmotic coefficient is so near to unity that it becomes doubtful whether the accuracy of the final result is improved by an extrapolation which involves placing equal reliance on the less accurate data for more dilute solutions, and in general molecular weights have been calculated from the osmotic pressure of approximate 1 per cent solutions. The best value for the osmotic molecular weight of crepe at 25° C is evidently that measured in benzene + 15% methyl alcohol, *viz.*, 2.2×10^5 . The agreement between the molecular weights found in the three solvents is very satisfactory, and confirms the validity of Ostwald's method of extrapolating the data for the solutions in benzene + 10% ethanol. Schulz's extrapolation formula (applied as in Part I by plotting $\Pi/c \sim \sqrt{\Pi}$) gives for this solvent $M = 4.0 \times 10^5$, and must, therefore, be definitely ruled out as inapplicable

to these solutions, if we assume the molecular weight to be independent of the solvent and equal to the above value of 2.2×10^5 . A plot of $\Pi/c \sim \Pi$, based on Sackur's equation, is only very approximately linear, but cannot be regarded as definitely disproved, since it leads to $M \approx 2.0 \times 10^5$.

Osmotic pressure measurements have been made on several other forms of raw rubber, benzene +15% methanol being employed as solvent. The results are collected in Table III.

The sol rubber was prepared from acetone-extracted crepe by diffusion into petrol ether (60-80). When 40 per cent had been extracted, further separation became very slow, and the remaining 60 per cent was taken as gel. Extractions with both acetone and petrol-ether were carried out in diffused light and in an atmosphere of nitrogen. Thanks are due to Mr. Grew for specimens of these materials. The rubber fractions were prepared by G. F. Bloomfield, by the methods described in a recent paper⁸, and were acetone-extracted before use. The importance of acetone extraction is indicated by the increase produced in the molecular weight of crepe from 2.2 to 2.6×10^5 . In the case of the low latex fraction, the effect was much more marked. Three samples were obtained, in

TABLE III
OSMOTIC MOLECULAR WEIGHTS OF RUBBERS

Material	$M \times 10^{-5}$
Crepe	2.2
Crepe (acetone-extracted)	2.6
Sol from acetone extracted crepe.....	3.0
Gel from acetone extracted crepe.....	2.1
Total latex rubber.....	2.8
Hydrocarbon from oxide fraction.....	0.66
Intermediate latex fraction.....	3.5
Low latex fraction.....	(2.1)

which the acetone extraction had been progressively more severe, and osmotic pressures measured in benzene +10% ethanol. It was at once apparent that the three samples were not comparable, so that extrapolation to infinite dilution could not be carried out in the usual way. Use was therefore made of the observation of Buchner and Steutel⁹ that the slopes of the $\Pi/c \sim c$ curves for a series of nitrocelluloses were independent of the molecular weight, and the $\Pi/c - c$ curve for the low latex fraction assumed to be parallel to that for crepe: no large error can be introduced by this assumption. The values of $10^{-5} M$ for the three samples were 0.8, 1.3 and 2.1. This effect of acetone extraction is evidently to be ascribed to the removal of low molecular components, which would seriously affect the osmotic pressure even if present in small amount, for it was shown that there was no corresponding change in the intrinsic viscosity of the material. The molecular weight of 2.1×10^5 recorded is naturally to be regarded as less reliable than the figures for the other materials.

It is to be noted that the molecular weight of gel rubber is found to be considerably lower than that of sol, a result which is in direct contradiction to the assumption frequently made that the insolubility of gel rubber in petroleum solvents arises from its high molecular weight¹⁰. It is evident from the work of Brönsted⁷ that high molecular weight is not sufficient to produce insolubility in the case of the polystyrenes, and the present results show that some further mechanism is needed to explain the sol-gel separation.

VISCOSITY MEASUREMENTS

The viscosities of dilute solutions of crepe in various solvents have been measured as described in Part I, the solutions being prepared in the same way as for osmotic experiments. Measurements were restricted to very dilute solutions, and it was, in general, found that the intrinsic viscosity

$$[\eta] = \frac{1}{c} \log_e (1 + \eta_{sp})$$

was almost independent of the concentration, so extrapolation to infinite dilution to obtain $[\eta]_0$ was readily carried out. Benzene was an exception in this respect, $[\eta]$, rising rapidly with c . Some typical results are given in Table IV, in which values of $[\eta]$ are calculated by taking c in grams per 100 cc. of solution.

TABLE IV
INTRINSIC VISCOSITY OF CREPE AT 25° C

Solvent	c_1	$[\eta]_1$	c_2	$[\eta]_2$	c_3	$[\eta]_3$	$[\eta]_0$
Benzene	0.0352	6.95	0.0300	6.70	0.0200	6.35	5.7 ₅
Ethylene dichloride	0.102	3.14	0.0500	3.14	0.0200	3.19	3.1 ₅
Amyl acetate	0.098	3.52	0.049	3.40	—	—	3.3 ₀
Benzene + 15% methanol	0.0503	3.28	0.0302	3.36	—	—	3.4 ₅
Benzene + 10% ethanol	0.0588	4.95	0.0200	4.83	—	—	4.8 ₀

TABLE V
EFFECT OF METHANOL ON INTRINSIC VISCOSITY OF RUBBERS

Material	$[\eta]_0$ Benzene	$[\eta]_0$ Benzene +15% methanol	Ratio
Crepe	5.7 ₅	3.4 ₅	0.60
Sol rubber	5.7 ₅	3.3 ₅	0.58
Intermediate latex fraction.....	5.8 ₀	3.5 ₀	0.60
Milled crepe	1.33	0.81	0.61
Hydrocarbon from oxide fraction..	1.02	0.60	0.61

The intrinsic viscosity evidently depends on the solvent and, in particular, the addition of small amounts of a nonsolvent reduces the viscosity considerably. The fact that different intrinsic viscosities are found in different solvents does not necessarily prevent their use in calculating molecular weights, as long as the ratio of the intrinsic viscosities in two solvents is independent of the molecular weight of the material so that a definite Staudinger constant can be applied to each solvent. Table V contains a comparison of some intrinsic viscosities measured in benzene and in benzene + 15% methanol and it will be noted that this relationship holds good.

In calculating the molecular weight by means of the Staudinger equation, it is, therefore, necessary to employ a separate constant for each solvent employed. Determination of the absolute value of this constant involves comparison with a molecular weight determined in some other way. Staudinger and Bondy¹¹ compared the viscosity and cryoscopic molecular weights of rubber-degradation products, of molecular weight approximately 4000, in tetralin and xylene solutions. Expressing the Staudinger equation in the form:

$$M = K[\eta]$$

and converting concentrations to grams of rubber per 100 cc. of solution, their constants¹² are found to be:

$$\text{Tetralin } K = 2.5 \times 10^4.$$

$$\text{Xylene } K = 2.9 \times 10^4.$$

From the data of Kemp and Peters¹⁰ for masticated crepe solutions, the constants for tetralin, benzene and hexane stand in the ratio 1:1.04:1.18, and the constant for benzene would then be 2.6×10^4 . Applying this to our data for the intrinsic viscosity of crepe leads to a molecular weight of 1.5×10^5 . This is to be compared with the osmotic value of 2.2×10^5 and, in view of the fact that the viscosity molecular weight must, for a nonhomogeneous material, be greater than the osmotic value (*cf.* Part I), it is evident that this constant is too small. Considering the very large extrapolation involved, the discrepancy is surprisingly small, but it would clearly be more satisfactory to compare directly the viscosity and molecular weight of a material of high molecular weight. The comparison should ideally be made for a homogeneous material or, alternatively, the molecular weight used should be a weight average. Lansing and Karemer¹³ have com-

TABLE VI
STAUDINGER CONSTANTS FOR RUBBER

Solvent	$10^{-4} K$
Ether	9.4
Benzene	6.0
Benzene + 15% methanol	10.2
Benzene + 10% ethanol	7.1
Ethylene dichloride	10.8
Amyl acetate	10.4
Tetralin	5.8
Hexane	6.8

pared the weight average molecular weight of sol rubber (determined by ultracentrifuge) with its intrinsic viscosity in ether solution with the following results:

$10^{-5} M_w$	$[\eta]$	$10^{-4} K$ (Staudinger)
4.0	4.21	9.5
4.3 _s	4.65	9.3 _s
Mean		9.4

The intrinsic viscosity of our sample of sol rubber in ether at 25° C was measured and found to be 3.65, whence using the above constant its weight average molecular weight¹⁴ is $3.4_3 \times 10^5$. Having now obtained the molecular weight of sol rubber, the Staudinger constants for benzene and benzene + 15% methanol can be calculated from the intrinsic viscosities given in Table V. Thence by use of Table IV, the constants for the various solvents employed for crepe are calculated. In Table VI these constants are tabulated, together with some for other solvents calculated from the ratios between viscosities in different solvents measured by Kemp and Peters¹⁰.

It is now possible to employ these constants to calculate the viscosity molecular weights of various forms of raw rubber, for comparison with the osmotic data given in Table III. The comparison is made in Table VII, which includes also values of the nonuniformity coefficient β , as defined by Lansing and Kraemer¹⁵.

In the absence of a precise knowledge of the molecular weight distribution, they assume it to be represented by an error function. The number and weight average molecular weights are then calculated in terms of the most probable molecular weight M_p and a single parameter β :

$$\begin{cases} M_n = M_p e^{0.75\beta^2} \\ M_w = M_p e^{1.25\beta^2} \end{cases}$$

whence

$$\beta^2 = 2 \log_e M_w / M_n$$

These results may now be employed to test the applicability of the Staudinger law to rubber solutions. If the rubber fractions separated by Bloomfield and Farmer were homogeneous, their osmotic and viscosity molecular weights should be equal. Hence, if the Staudinger law holds, the ratio of osmotic molecular weights to intrinsic viscosity in a given solvent should be the same for all the

TABLE VII
VISCOSITY AND OSMOTIC MOLECULAR WEIGHTS OF RUBBER

Material	10 ⁻⁵ M		Solvent used for viscosity measurement	β
	Osmotic	Viscosity		
Crepe	2.2 ± 0.1	3.4 ₅ ± 0.1	Benzene	1.0 ₅ to 0.8 ₅
Acetone-extracted crepe.	2.6 ± 0.2	3.4 ₅ ± 0.1	Benzene	0.9 to 0.6
Sol from acetone-ex-	3.0 ± 0.2	3.4 ₅ ± 0.1	Ether	0.7 to 0.3
tracted crepe				
Gel from acetone-ex-	2.1 ± 0.1	3.0 ₅ ± 0.1	Benzene + 15% methanol ...	0.9 ₅ to 0.8
tracted crepe				
Total latex rubber.....	2.8 ± 0.2	3.3 ± 0.1	Benzene + 15% methanol ...	0.7 ₅ to 0.3 ₅
<i>Rubber Fractions</i>				
Hydrocarbon from oxide	0.66 ± 0.03	0.63 ± 0.02	Benzene	—
fraction				
Low latex fraction.....	2.1 ± 0.3	2.4 ± 0.1	Benzene	—
Intermediate later frac-	3.5 ± 0.2	3.5 ₅ ± 0.1	Benzene + 15% methanol ...	—
tion				

fractions, and equal to the Staudinger constant. If further, the scale of Staudinger constants drawn up in Table VI is correct, the viscosity molecular weights of the fractions calculated from them should agree with their osmotic molecular weights. It is evident from Table VII that this is true, within experimental error, and we may therefore draw two important conclusions. (1) The Staudinger law holds for rubber solutions at least over the molecular weight range 60,000 to 350,000. (2) The scale of constants given in Table VI may be employed to calculate absolute weight average molecular weights from intrinsic viscosities measured in dilute solution.

The following consideration suggests that the limits of validity of the Staudinger law are by no means defined by the above figures. Taking the constant obtained for tetralin (Table VI), the viscosity molecular weight of the degraded rubber used as a standard by Staudinger is 8,000, which is to be compared with the cryoscopic value of 3,400. The difference is accountable on the basis of a β of 1.3, not an unreasonable value for a degraded product. It appears safe, therefore, to conclude that the Staudinger law holds to a good approximation, even down to this molecular weight, and thus to apply it with considerable confidence to less degraded products.

The discrepancy between the osmotic and viscosity molecular weights for nonfractionated rubbers is to be expected on the grounds of their heterogeneity. The progressive approach to homogeneity in the first three materials of Table VII is reflected in the decreasing β values, while gel rubber is seen to be much less homogeneous than sol.

SUMMARY

The osmotic molecular weight of crepe has been measured in several solvents. It is shown that the use of a poor solvent, or a mixture of solvent and precipitant, gives solutions which approach ideal osmotic behavior. Benzene containing 150 cc. of methanol per liter is the best solvent examined, 1 per cent solutions of crepe being almost ideal.

Viscosity data are employed to calculate absolute weight average molecular weights, the Staudinger constant being determined by comparison with ultracentrifuge data. Constants are listed for a number of solvents, and shown to vary only by a small factor.

The osmotic and viscosity molecular weights of a number of rubbers are compared; the two values agree for three rubber fractions, while for unfractionated materials the viscosity average is the higher. Non-uniformity coefficients are calculated from the ratio of the two molecular weights.

The molecular weight of sol rubber is higher than that of gel, showing that the sol-gel separation does not arise from molecular weight difference.

The Staudinger law is shown to hold for rubber solutions at least over the molecular weight range 350,000—60,000, and probably very much further.

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- ¹² All Staudinger constants in this paper are defined by the equation: $M = K [\eta]$, and are therefore inversely proportional to the K_m values usually employed.
- ¹³ Busse in "The Chemistry and Technology of Rubber", Edited by Davis and Blake, New York, 1937, p. 232.
- ¹⁴ Ether is a very unsatisfactory solvent for a viscosity molecular weight standard for two reasons: (1) its high volatility makes it difficult to make accurate viscosity measurements at 25° C; (2) it very readily develops peroxides which would lead to degradation of the rubber. The solvent used was free from peroxides, and the solution was made in vacuo as usual. To minimize the effect of evaporation, the viscosity determinations were made as rapidly as possible.
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VISCOSITY-MOLECULAR WEIGHT OF RUBBER

CRYOSCOPIC DEVIATION OF RUBBER SOLUTIONS FROM RAOULT'S LAW *

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Considerable attention has recently been given to the Staudinger viscosity-molecular weight method because of its simplicity and possible application to a wide variety of high polymers. Numerous questions, however, have been raised regarding the influence of several variables on the results by the method, and there appears to be little agreement in respect to the most suitable equation for calculating the average molecular weight from viscosity data.

The purpose of the present paper is to help clear up some of these questions and to provide a more satisfactory basis than now exists for the estimation of the average molecular weight of rubber and related substances. In the present work the Staudinger¹⁴ viscosity-molecular weight relation is critically examined, and various solvents and procedures for determining the molecular weight of rubber by the viscosity method have been studied.

In this, as in a previous study⁷, the solutions were prepared by diffusion methods and shaking was avoided to obtain true molecular dispersion and avoid inclusion of gel particles or molecular aggregates which may occur on violent agitation. An Ostwald viscometer was employed, and the temperature held at $25^{\circ}\text{C} \pm 0.10^{\circ}$. This control of temperature is satisfactory, since the difference in the relative viscosity of dilute rubber sols at 20° and 25°C is practically nil. The length of the capillary of the viscometer used was 10.3 cm. and its diameter 0.066 to 0.067 cm.† This viscometer agreed closely with the dimensions set by the British Standards Institution³ for the No. 1 Ostwald type.

Using exactly 5 cc. of solution, the time of flow in seconds for some pure liquids at 25° were: distilled water 95.2, *n*-hexane 50.7, cyclohexane 120.2, benzene 72.5, chloroform 40.0, toluene 68.0, carbon tetrachloride 60.1.

VISCOSITY-MOLECULAR WEIGHT EQUATIONS

Staudinger's equation¹⁴ is applicable only to linear polymers of known structure, and is based on the assumption that, in very dilute solutions of high polymers having viscosities below certain critical values, the individual polymeric molecules are dispersed without mutual interference. Under this condition, Staudinger claimed that the specific viscosity divided by the concentration is a constant. By determining this constant with low polymers of known molecular weight, the effect of each base-mole of the polymer on the viscosity was determined. Staudinger then employed Equation 1 to calculate a molecular weight conversion factor, K_m , for the particular polymer under investigation. The

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† In a previous article⁷ the diameter was erroneously given as 0.066 to 0.067 mm.

average molecular weight, M , of mixtures of high polymers of the same substance were then calculated from viscosity data on dilute solutions:

$$M = \eta_{sp}/(CK_m) \quad (1)$$

It has not yet been definitely proved, however, that the same relation holds for polymers having high molecular weights, since no independent method is available to determine the average polymeric size of such substances with sufficient accuracy.

Contrary to Staudinger's claim, an examination of the extensive published data on the viscosity of solutions of numerous high polymers shows that η_{sp}/C

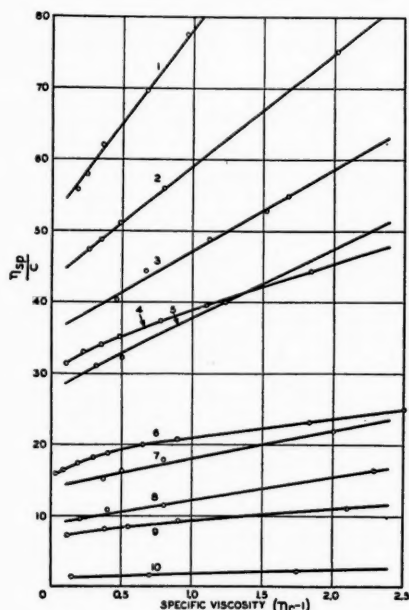


FIG. 1.—Variation in η_{sp}/C with viscosity of dilute solutions of high polymers.

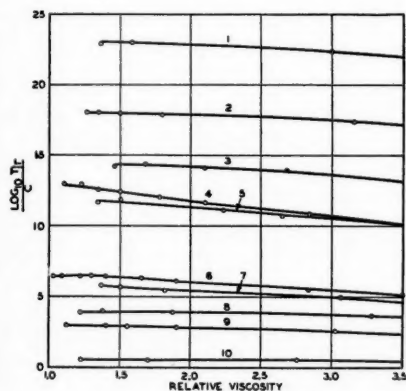


FIG. 2.—Variation in $\log \eta_r/C$ with viscosity of dilute solutions of high polymers.

1. Rubber in chloroform
2. Rubber in hexane
3. Polyisobutylene in hexane
4. Polystyrene in benzene
5. Rubber in hexane
6. Polyester of W-hydroxyundecanoic acid² in chloroform
7. Gutta-percha hydrocarbon in benzene
8. Masticated rubber in hexane
9. Polystyrene in benzene
10. Depolymerized rubber in hexane

steadily decreases with decreasing concentration, even in dilute solutions at low viscosity levels. In the case of extremely dilute solutions of rubber hydrocarbon, large variations in the calculated molecular weights were found⁷ over a fairly narrow viscosity range when the Staudinger equation was employed. The variation of η_{sp}/C is shown in Figure 1 for various polymer solutions varying in molecular weight level. It is seen that the higher the molecular weight, the higher the slope of η_{sp}/C plotted against η_{sp} .

Staudinger also used Equation 2 based on the Arrhenius¹ relation, $\log \eta_r/C = K_c$:

$$M = \log \eta_r \times K_{cm}/C \quad (2)$$

Although Staudinger and others appear to have favored Equation 1, it is evident that Equation 2 is to be preferred, since $\log \eta_r/C$ is constant over a fairly wide viscosity range; this is evident in Figure 2, in which $\log \eta_r/C$ is plotted against η_r for a number of solutions of different polymeric substances. In this

case the slope of these lines is small and quite uniform with variations in molecular weight level. The slope for high molecular polystyrene differs somewhat, possibly because it may not be strictly a linear polymer but a branched-chain one, as recently pointed out by Schulz¹².

Since K_m varies with viscosity, this variation is given by the following expressions:

$$\frac{\eta_{sp}}{CK_m} = \frac{\log \eta_r \times K_{cm}}{C}$$

or

$$K_m K_{cm} = \frac{\frac{\eta_{sp}}{C}}{\frac{\log \eta_r}{C}} = \frac{\eta_{sp}}{\log \eta_r}$$

at a given concentration. The greater constancy of $\log \eta_r/C$ compared with η_{sp}/C was also pointed out by Hess and Sakurada⁵ in the case of chloroform and cresol solutions of cellulose acetate. They showed mathematically that at zero concentration:

$$K_{cm} = \frac{2.3023}{K_m}$$

or

$$\frac{\eta_{sp}}{\log \eta_r} = 2.3023$$

To show the variation of K_m with relative viscosity or concentration, $\eta_{sp}/\log \eta_r$ or $K_m K_{cm}$ is plotted in Figure 3 against η_r in a range of 1 to 5. Extrapolation to η_r of 1.0 gives a $K_m K_{cm}$ value of 2.30, as shown by Hess and Sakurada. To avoid serious error in using the Staudinger equation, it will therefore be necessary to select a fixed viscosity at which the K_m value is determined and used. By using Figures 1 and 2, it is possible to extrapolate the values of η_{sp}/C or $\log \eta_r/C$ to indefinite dilution; however, this may not always be accurate, since the slopes of the η_{sp}/C curves apparently change for very dilute solutions.

Since $\log \eta_r/C$ has been shown experimentally to be independent of concentration within narrow limits, it is obvious that Equation 2 is subject to less discrepancy when solutions of varying viscosity levels are concerned than is Equation 1.

DETERMINATION OF VISCOSITY-MOLECULAR WEIGHT CONSTANTS

The values given in the literature for K_m and K_{cm} for various high polymers are sometimes questionable as to accuracy. The difficulty arises from the lack of polymeric substances of known structure having moderately high molecular weights in a narrow distribution range. In the case of polyprenes with molecular weights up to 5000 or somewhat higher, Staudinger employed the ordinary cryoscopic method, using benzene to determine the K_m value. Other independent methods are not available to determine molecular weights of hydrocarbons accurately in this range, as in the case of some substances with active end groups. Several investigators have found that the molecular weight of crepe rubber obtained by the osmotic method gives only proximate values at best.

In Table I, Staudinger's data for low-molecular polyprenes and polypranes are used to calculate K_m and K_{cm} . The largest variations in the K_m values are due to differences in viscosity levels of the solutions measured. Details are lacking in respect to the molecular weight distribution range of these substances. In Staudinger's work, the rubber and gutta were broken down by refluxing for long periods in solvents, and the polymer was then precipitated from the solutions with alcohol, which removed the resins and low-polymer fraction. Traces of solvents were removed by heating under vacuum.

The presence of residual solvent and low-molecular substances must be strictly eliminated, and the polymer size distribution range must be sufficiently narrow or large errors will result in cryoscopic measurements. For example, it is calculated that in a mixture of 50 per cent of a polymer of 1000 molecular weight

TABLE I
VISCOSITY-MOLECULAR WEIGHT CONSTANTS FOR POLYPRENE BY STAUDINGER¹³

Substance	Cryo- scopic mol. wt. ^a	Concn., base mole	η_r	$\frac{\eta_{sp}}{C}$	$\frac{\text{Log } \eta_r}{C}$	$K_m \times 10^4$	$K_{cm} \times 10^{-4}$	$K_m K_{cm}$
Polyprene (rubber)	3300	0.25 ^b	1.26	1.04	0.402	3.15	0.82	2.58
		0.50	1.55	1.10	0.381	3.33	0.87	2.89
		1.00	2.29	1.29	0.360	3.90	0.93	3.62
	4200	0.25 ^b	1.29	1.16	0.442	2.76	0.95	2.62
		0.50	1.66	1.32	0.440	3.14	0.95	3.00
		1.00	2.83	1.83	0.452	4.36	0.93	4.05
Polyprene (gutta-percha). 6500	6500	0.25 ^b	1.50	2.00	0.704	3.07	0.93	2.85
		0.50	2.15	2.30	0.665	3.54	0.98	3.47
		1.00	4.30	3.30	0.633	5.07	1.03	5.22
Polyprane (rubber)	4575	0.10 ^c	1.12	1.20	0.492	2.60	0.93	2.44
		0.25	1.31	1.24	0.469	2.71	0.97	2.62
		0.50	1.72	1.44	0.471	3.15	0.97	3.05
	2850	0.5 ^b	1.46	0.92	0.329	3.23	0.92	2.81
		1610	0.5 ^b	1.24	0.48	0.187	3.00	0.86
	Polyprane (gutta-percha). 5350	5350	0.5 ^c	1.41	1.48	0.481	3.26	0.90

^a Cryoscopic measurements in benzene.

^b Solution in benzene.

^c Solution in tetralin.

and 50 per cent of one of 6000, the K_m constant, determined from cryoscopic molecular weight values, is double that found if the polymer is all 3500. Likewise the K_{cm} value is cut in half. Since it is difficult to prepare uniform polymers, the importance of the distribution effect cannot be overemphasized.

The averaging of all results on polyprene and polyprane in Table I gives a value for K_m of 3.32×10^{-4} and for K_{cm} of 0.94×10^4 , at an average η_r of 1.83. Staudinger selected the values of 3×10^{-4} for K_m and 10^4 for K_{cm} , which appear to be approximately correct at a relative viscosity of 1.66. At infinite dilution, however, K_m should be lowered, and under this condition a K_m value of 2.45×10^{-4} , with a K_{cm} value of 0.94×10^4 , would be a proper selection.

It is important that Staudinger's values for K_m and K_{cm} be carefully checked, since the absolute molecular weight values depend on their reliability. To do this, a low-polymeric liquid rubber was prepared by refluxing 250 grams of purified crepe in 450 grams of tetralin for 11 hours at 202° C. The tetralin was then distilled off over a period of 5 hours, the final temperature rising to 240° C. The

product was washed three times by shaking with warm acetone. It was then dissolved in hexane and partially precipitated by adding acetone. After settling, the solution was decanted, the solvent was removed on the steam bath, and the products were heated to constant weight at 100° C. under a high vacuum to remove the last traces of solvent. This process of solution and partial precipitation was repeated twice, and the final precipitated residue was dissolved in hexane, leaving a small fraction which was insoluble. For some unknown reason, when Fractions 7 and 8 were heated at 100° under a vacuum, they became insoluble in benzene and chloroform, and were elastic like soft, partially vulcanized rubber.

Data on the fractionation of this rubber, including the K_c values of the different fractions determined in benzene, are summarized in Table II. Table III gives more detailed cryoscopic data for these fractions in comparison with similar data on other preparations to be described later. The cryoscopic molecular weights were determined with Kahlbaum's or Eastman's thiophene-free benzene or a highly purified cyclohexane furnished by the Barrett Company and used for vitamin assay by infrared absorption. The high purity of this cyclohexane is

TABLE II
FRACTIONATION OF DEPOLYMERIZED RUBBER

Fraction	Per cent	$K_c = \log \eta_r / C$	Remarks
Original material.	—	0.666	Brown viscous liquid
1. acetone-sol.	2.2	0.166	Somewhat viscous yellow liquid
2. acetone-sol.	7.0	0.177	
3. acetone-sol.	4.5	0.175	
4. from pptn.	28.6	0.545	Clear yellow viscous liquid
5 ^a . from pptn.	25.8	0.718	
6. from pptn.	12.8	0.711	
7. Hexane-sol. portion of ppt. 6.	15.8	Insol. ^b	Brown elastic solid
8. Insol. residue of ppt. 6.	3.3	Insol. ^b	Brown elastic solid

^a Analysis of fraction 5: C, 86.86 and 86.65 per cent; H, 11.39 and 11.60; O (by difference), 1.75 and 1.75; iodine value, 842.

^b Became insoluble on heating under a vacuum at 100° C.

shown from the constant temperature during extensive crystallization on cooling. Its density at 20° C was 0.7783, and its freezing point was found to be 6.56° C. The use of cyclohexane is advantageous since its molecular freezing point constant is 20.2 instead of 5.1 for benzene, which gives greater accuracy.

The iodine value of melted rubber fraction 5 proves that it is not cyclized. The iodine value is consistent with the oxygen content, and shows that some oxygen has combined with the polymer.

If the cryoscopic results in Table III on Fractions 4, 5, and 6 are averaged, and if the values for η_{sp}/C and $\log \eta_r/C$ are taken nearest the relative viscosity of 1.7, the average K_{cm} and K_m values are calculated to be 0.92×10^4 and 3.30×10^{-4} , respectively. The agreement with Staudinger's results in Table I, using similar preparations at the same viscosity, is thus seen to be satisfactory. As would be expected, however, the unfractionated material gives high K_m and low K_{cm} values, due to the presence of low polymers and wide distribution, which will yield lower cryoscopic values than the average molecular weight calls for.

Since Fraction 3 behaved ideally in respect to Raoult's law and 4, 5, and 6 did not, several other low-molecular fractions were prepared from depolymerized rubber by warm acetone extraction, followed by washing the extracted polymer with methanol to remove the resin and extremely low polymers. Analysis of

TABLE III
 VISCOSITY-MOLECULAR WEIGHT CONSTANTS OF DEPOLYMERIZED RUBBER

Solvent	Concentration		η_r	$\frac{\text{Log } \eta_r}{C}$	$\Delta^\circ_1 - \Delta^\circ_2$	Cryo- scopic mol. wt.	$K_m \times 10^4$	$K_{em} \times 10^{-4}$	$K_m K_{em}$
	Base moles	G./100 g. solvent							
ORIGINAL MATERIAL									
C_6H_6	0.200	1.18	1.363	0.673	0.011	5,480	3.32	0.81	2.68
	0.300	2.38	1.584	0.666	0.026	4,670	4.17	0.71	2.92
	0.600	4.86	2.382	0.628	0.071	3,510	6.56	0.56	3.68
	1.200	10.19	4.690	0.559	0.184	2,840	10.9	0.51	5.56
FRACTION 3									
C_6H_6	0.206	1.62	1.084	0.170	0.074	1,120	3.64	0.66	2.40
	0.412	3.29	1.178	0.173	0.141	1,200	3.60	0.69	2.48
	0.823	6.78	1.394	0.175	0.292	1,190	4.00	0.68	2.72
FRACTION 4									
C_6H_6	0.353	2.83	1.559	0.545	0.028	5,160	3.06	0.95	2.91
	0.707	5.75	2.296	0.510	0.069	4,280	4.28	0.84	3.58
C_6H_{12}	0.170	1.58	1.266	0.602	0.053	6,020	2.59	1.01	2.61
	0.340	3.21	1.594	0.595	0.130	4,990	3.51	0.84	2.95
	0.680	6.60	2.382	0.543	0.325	4,100	4.95	0.76	3.76
FRACTION 5									
C_6H_6	0.180	1.42	1.363	0.747	0.009	8,060	2.50	1.08	2.70
	0.360	2.86	1.813	0.718	0.023	6,360	3.54	0.89	3.14
	0.720	5.87	2.993	0.660	0.058	5,190	5.32	0.79	4.20
C_6H_{12}	0.181	1.60	1.364	0.745	0.040	8,050	2.50	1.08	2.70
	0.361	3.23	1.841	0.732	0.098	6,660	3.49	0.90	3.14
	0.722	6.65	3.101	0.678	0.260	5,160	5.64	0.76	4.28
FRACTION 6									
C_6H_{12}	0.352	3.15	1.788	0.711	0.095	6,740	3.31	0.94	3.11
	0.705	6.50	2.965	0.665	0.242	5,430	5.10	0.82	4.16
ACETONE-SOL. PORTION WASHED WITH ALCOHOL									
C_6H_6	0.143	1.12	1.064	0.191	0.041	1,410	3.17	0.74	2.35
	0.287	2.26	1.132	0.187	0.085	1,370	3.35	0.73	2.43
	0.573	4.62	1.287	0.189	0.180	1,310	3.82	0.69	2.62
	1.146	9.70	1.662	0.190	0.405	1,220	4.73	0.64	3.10
ACETONE-SOL. PORTION REWASHED WITH ALCOHOL									
C_6H_6	0.114	0.89	1.058	0.215	0.022	2,060	2.47	0.96	2.37
	0.228	1.80	1.113	0.204	0.051	1,800	2.78	0.88	2.42
	0.457	3.65	1.235	0.201	0.119	1,570	3.27	0.78	2.55
	0.914	7.58	1.525	0.201	0.267	1,450	3.96	0.72	2.85
C_6H_{12}	0.149	1.33	1.070	0.197	0.165	1,620	2.90	0.83	2.41
	0.299	2.69	1.145	0.197	0.323	1,670	2.88	0.85	2.50
	0.598	5.47	1.326	0.205	0.649	1,700	3.20	0.83	2.66
ACETONE-SOL. PORTION OF MELTED RUBBER WASHED WITH ALCOHOL									
C_6H_6	0.146	1.14	1.051	0.150	0.048	1,220	2.86	0.81	2.31
	0.291	2.30	1.113	0.160	0.091	1,300	2.98	0.80	2.38
	0.583	4.70	1.244	0.163	0.199	1,210	3.48	0.74	2.57
	1.165	9.86	1.546	0.163	—	1,240 (av.)	3.77	0.76	—
PREPARATION 2, FRACTION 2									
C_6H_{12}	0.120	1.07	1.307	0.97	0.007	30,870	0.82	3.18	2.61
	0.240	2.13	1.681	0.94	0.030	14,300	1.98	1.52	3.00
	0.480	4.35	—	—	0.087	10,100	—	1.05	—
	0.639	5.86	—	—	0.147	8,070	—	0.84	—
	0.959	9.00	—	—	0.301	6,050	—	0.63	—

this material gave the following results: carbon 83.12 per cent, hydrogen 10.94, oxygen (by difference) 5.94; C:H ratio 1.59; iodine value 307.

In the case of Fraction 2 (preparation 2) crepe was first extracted with a mixture of equal volumes of acetone and η -hexane. The solvent was removed and the rubber was broken down on cool rolls for 1 hour. Fifty grams were dissolved in 1 liter of benzene, and refluxed for 7 days. Acetone was then added to precipitate the higher fraction, 1500 cc. being required to complete the precipitation. The solution was decanted and evaporated to 250 cc., and an equal volume of acetone was then added to precipitate a second fraction, which was employed in this study. The yields and K_c values of these fractions were as follows:

Substance	Yield (per cent)	$K_c = \log \eta_r / C$
Original material	100	1.87
Fraction 1	75	2.24
Fraction 2 ^a	14	0.90
Fraction 3	11	0.61

^a Analysis of Fraction 2: C 86.98, H 11.60, O (by difference) 1.43; C:H ratio 1.61; iodine value 368.

Staudinger's practice was to determine molecular weights of low-polymeric rubber, polystyrene, etc., by the cryoscopic method in benzene, employing a concentration of 1 to 3 grams of solute for 100 grams of solvent. The difference in concentration was usually less than this in duplicate measurements on individual polymer preparations, and therefore his results did not reveal a concentration effect. The present authors have not found any data in the literature showing the concentration effect on cryoscopic measurements of low polymers of varying molecular weight. This effect apparently is a function of chain length of the polymer, and is not confined to rubber, since we have found that low polymers of isobutylene also show this effect.

Table III indicates in the case of the higher molecular weight Fractions 4, 5, and 6 that our results check those of Staudinger if the cryoscopic results at the lower concentrations are employed. However, in the case of Fraction 2, preparation 2, this is not true, since the molecular weight, calculated at the low concentration, is much higher than any rubber fraction employed by Staudinger.

In view of the results given in Table III and plotted in Figure 4, the values for K_m and K_{cm} selected by Staudinger cannot be accepted. A noticeable deviation from Raoult's law is evident in the case of a polymeric fraction with cryoscopic values in the neighborhood of 1400. A polyprene having a molecular weight of 1200 apparently behaves ideally, judged by the present results. The deviation from Raoult's law becomes greater as the chain length increases.

This observed deviation from Raoult's law in the case of the higher polymers is opposite from the changes which would be caused by association of polymer molecules as the concentration is increased. It bears a resemblance to the concentration dependence observed by Meyer and van der Wyk¹¹ for vapor pressure, osmotic pressure, and similar colligative properties of polymer solutions and ascribed by them to segment action of the chain.

If K_{cm} is calculated from the data on the lower polyprene fractions taken from Table III, the values range from 0.68 to 0.84×10^4 , the average being 0.77×10^4 . It is also of interest to note that, if the cryoscopic molecular weight values of all fractions are taken from Figure 4 where the curve cross 6 in the concentration ordinate, the calculated K_{cm} values range from 0.67 to 0.84×10^4 , with an average of 0.79×10^4 .

The average K_{cm} value for the low polymers whose solutions obey Raoult's law is found to be 0.75×10^4 , and this value has therefore been selected as the best to use in Equation 2 for calculating the molecular weight of benzene sols of crude rubber in the range of relative viscosities of 1.2 to 2.0. This value is 25 per cent lower than Staudinger's K_{cm} of 10^4 .

Staudinger and Mojen¹⁵ gave data for squalene ($C_{30}H_{50}$) and hydrosqualene ($C_{30}H_{62}$) in benzene at relative viscosities ranging from 1.12 to 1.16, from which the K_{cm} constant can be calculated. K_{cm} for squalene is found to be 0.65×10^4 and for hydrosqualene, 0.67×10^4 , which are in good agreement with the average values obtained in the case of the lower rubber polymers given in Table III.

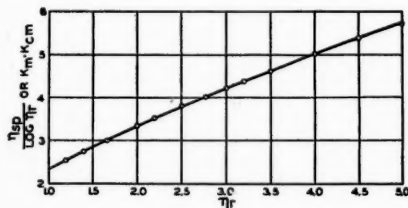


FIG. 3.—Relation between $\eta_{sp}/\log \eta_r$ or K_{cm} , K_{cm} , and η_r for solutions or high polymers.

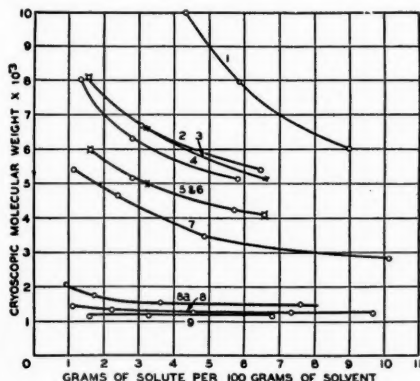


FIG. 4.—Effect of concentration on freezing point of low-molecular polyrenes of various chain lengths.

Curve no.	Polyprene	Solvent	Viscosity—mol. wt. ^a
1	Preparation 2, fraction 2	C_6H_{12}	7000
2	Preparation 1, fraction 6	C_6H_{12}	5000
3	Preparation 1, fraction 5	C_6H_{12}	5500
4	Preparation 1, fraction 5	C_6H_6	5500
5	Preparation 1, fraction 4	C_6H_{12}	4500
6	Preparation 1, fraction 4	C_6H_6	4100
7	Original material	C_6H_6	5000
8	Washed acetone-solubles	C_6H_6	1400
8a	Rewashed acetone-solubles	C_6H_6	1500
9	Preparation 1, fraction 3	C_6H_6	1300

$$^a M = \frac{\log \eta_r}{C} \times 0.75 \times 10^4.$$

Recent investigations by Baker, Fuller, and Heiss² accord with a trend, in the case of squalene and the present results, indicating that K_{cm} is not truly independent of molecular weight, but shows a decrease at low chain lengths. Hence the value 0.75×10^4 for K_{cm} derived from cryoscopic measurements of relatively low molecular weights should possibly be revised upward somewhat for very long chain rubber molecules.

Staudinger and Staiger¹⁷ determined the viscosities of pure paraffin hydrocarbons, C_nH_{2n+2} , in benzene, where n ranged from 27 to 35, and from these data the value of K_{cm} is calculated to be 2.45 to 2.62×10^4 , with an average of 2.56×10^4 . Since Staudinger's rule states that the viscosities of equimolar solutions of linear polymers are proportional to their chain lengths, it is possible to calculate the K_{cm} value of rubber from that of paraffin by considering the relative lengths of the base molecules of both substances. These lengths are 1.25 Å.

for paraffin and 4.65 Å. for rubber, calculated from planar chains, assuming normal valence angles and bond distances. Therefore, $(1.25/4.65) \times 2.56 \times 10^4 = 0.70 \times 10^4$, which agrees closely with our experimentally determined K_{cm} value for rubber. This agreement may be somewhat fortuitous since the above relation may not strictly hold in solution.

Gee⁴ recently measured the viscosity of a crepe sol in benzene; using the formula $M = K(\eta)$ with a K value of 2.6, he obtained a molecular weight of 150,000. Since (η) is equal to $\log \eta_r/C \times 2.3$, this K should be equal to Staudinger's $K_{cm} \times 2.30$. It was claimed that the above molecular weight value is too low, since osmotic pressure measurements on a resin-free rubber sol gave a molecular weight value of 300,000. Gee obtained a higher K value by basing his calculations on molecular weights obtained by Lansing and Kraemer⁸ from ultracentrifuge measurements made on an ether sol of rubber. By this procedure the average viscosity-molecular weight of benzene sol from crepe was estimated to be 340,000, a value which reflects the high value obtained by the ultracentrifuge method. It is of interest to note that a molecular weight value of 60,000 was cited by Mark¹⁰ for a toluene solution of rubber, determined by the ultracentrifuge method. Since the ultracentrifuge method gives widely varying results, it has not been generally accepted for application to rubber sols, and therefore Gee's procedure is questionable.

Assuming uniform distribution of polymeric weights in rubber, the number average molecular weight given by the osmotic method is approximately one-half the weight average given by the viscosity procedure⁹. Therefore, if Gee's osmotic pressure results are accepted as satisfactory, the value for the weight average molecular weight for benzene sol is approximately 560,000; this is much higher than the value of approximately 150,000 which we obtained⁶ by employing a K_{cm} of 0.75×10^4 in the viscosity-molecular weight Equation 2.

Gee reported values of (η) of 6.95 and 6.70 for benzene solutions of crepe, (η) having been determined as $\log_e \eta_r/C$, in grams per 100 cc. of solution. The average of these values, 6.82, is converted to $\log_{10} \eta_r/C$ (in base moles) by dividing it by 0.338, which gives a $\log_{10} \eta_r/C$ value of 20. If this is divided into Gee's weight average osmotic value for resin-free crepe of 560,000, we obtain a K_{cm} value of 2.8×10^4 , which is four times the value arrived at in the present investigation. This result raises a question as to the probable accuracy of molecular weight values of rubber sols determined by the osmotic method which apparently gives inordinately high values. The failure of high-polymeric rubber solutions to obey Raoult's law probably accounts for these high osmotic values.

SOLVENT EFFECTS

The addition of polar substances, such as alcohol or ketones, to a poor rubber solvent such as hexane, within certain limits, increases the solvent power of the latter considerably. Similar additions to a good solvent such as benzene, chloroform, or carbon tetrachloride have a less pronounced effect. Since the addition of a polar solvent to rubber sols in non-polar solvents causes large reductions in viscosity, their use is not permissible in viscosity-molecular weight work unless standardization with known low polymers is first established. Even this appears difficult, since a greater effect is found when a polar solvent is added to a solution of rubber of high molecular weight than when added to a solution of low molecular weight. Staudinger¹⁴ pointed out that the viscosity method as applied to hydrocarbons does not permit the use of highly polar or chemically active solvents.

The fact that certain solvents yield different viscosities with the same concentration of a given sample of rubber has been the basis of adverse comment on the Staudinger method.

Differences in the internal structure of the solvents as well as the solute might be expected to affect the shearing resistance between the polymer and different types of solvent molecules. Exact knowledge regarding solution structure and mechanism of "solvent effects" on the viscosity of high polymers in solution is lacking. Staudinger has been aware of the solvent effect, but in many instances the same viscosity-molecular weight constant has been employed with different solvents without consideration of this point.

This so-called solvent effect is important, and often in the case of rubber the method of preparing the solutions and the greater tendency of rubber to break down in one solvent, compared with another, leads to variable viscosity in different solvents for the sample of rubber.

Since crude rubber is not completely soluble in any known solvent, the insoluble gel has undoubtedly been a disturbing factor in viscosity measurements of whole rubber reported by numerous investigators.

To throw more light on this subject, comparative measurements were made of the viscosities of various rubber fractions diffused into different solvents compared with benzene as standard. These results are given in Table IV. With the exception of hexane and Tetralin, the solvents show little difference in $\log \eta_r/C$ values of high-molecular polyprenes. In the case of the lower polymers, both chloroform and carbon tetrachloride give higher results than benzene. These results indicate that the same K_{cm} constant can be used for solutions of the high polymers in various solvents except in the case of tetralin, which is unsatisfactory, and hexane which requires a higher constant. The use of hexane or cyclohexane is not satisfactory for rubber fractions of extremely high molecular weight, since they are not appreciably soluble in these solvents. Benzene or toluene are recommended for general use. For high-polymeric rubber and in the study of crude rubber, chloroform is the preferred solvent, as will be shown later⁶.

In view of these results, it becomes evident that solvents must be carefully chosen and studied in great detail with each polymeric series if the viscosity-molecular weight method is to be made reliable.

Staudinger and Mojen¹⁶ compared the viscosities of masticated crepe in several solvents. Their $\log \eta_r/C$ values, in comparison with benzene as 100, were calculated to be 124 for carbon tetrachloride, 103 for tetralin, and 108 for cyclohexane. These values are in fair agreement with those in Table IV. It has been noted that, because of limited solubility, a high polymer may give a different solvent effect in a given solvent from that of the same substance in a lower state of polymerization. A polymer may be swollen and molecularly dispersed in a so-called good solvent, but in a poor solvent the dispersion may contain molecular aggregates.

By the use of good nonpolar solvents, such as benzene or toluene, and by careful preparation of the solution by diffusion methods in the absence of light and oxygen, highly reproducible results can be obtained in the case of polyprenes showing a wide range of molecular sizes.

Evidence is accumulating that the Staudinger viscosity rule holds under certain specified conditions for linear polymers. The evidence on this point in the case of polyprenes is still lacking. However, by proper procedure results are obtained which are of considerable value in the study of various types of rubber.

TABLE IV
EFFECT OF VARIOUS SOLVENTS ON THE VISCOSITY OF RUBBER

Substance	Solvent	Concn., base mole	η_r	$\frac{\log \eta_r}{C}$	Ratio $\log \eta_r/C$ values (benzene =100)
Depolymerized crepe (unfractionated)	Benzene	0.3897	1.796	0.653	100
	Chloroform	0.3239	1.735	0.739	113
	Cyclohexane	0.3176	1.613	0.654	100
	Hexane	0.4134	1.679	0.544	83
Depolymerized crepe (Fraction 4)	Benzene	0.353	1.559	0.545	100
	Cyclohexane	0.360	1.594	0.563	104
	Chloroform	0.294	1.510	0.609	112
Depolymerized crepe (Fraction 5)	Benzene	0.362	1.813	0.713	100
	Cyclohexane	0.362	1.841	0.732	103
	Hexane	0.363	1.647	0.597	84
Masticated crepe (11 min. on cool rolls)	Benzene	0.500	1.742	4.82	100
	Chloroform	0.500	1.832	5.25	109
	Hexane	0.500	1.601	4.09	85
Masticated crepe (25 min. on cool rolls)	Benzene	0.833	1.884	3.30	100
	Tetralin	0.833	1.864	3.25	99
	Hexane	0.833	1.779	3.00	91
Pure gutta-percha hy- drocarbon	Benzene	0.0470	1.822	5.54	100
	Toluene	0.0470	1.878	5.82	105
	Chloroform	0.0500	2.050	6.24	113
	CCl ₄	0.0500	2.150	6.65	120
2nd hexane fraction from resin-free crepe	Benzene	0.01209	1.618	17.3	100
	Toluene	0.01209	1.626	17.4	101
	Hexane	0.01343	1.586	15.1	87
	Cyclohexane	0.01209	1.605	17.0	98
	CCl ₄	0.01209	1.646	17.9	103
	Chloroform	0.01209	1.608	17.1	99
	Tetralin ^a	0.01209	1.521	15.1	(87)

^a Unsatisfactory solvent for high-polymeric rubber shows increasing rate of flow on repeated runs (7).

TABLE V
VISCOSITY-MOLECULAR WEIGHT OF CREPE SOL IN CHLOROFORM

Concn. (base mole)	η_r	M values		
		$\frac{\eta_{sp}}{C \times 10^{-4}}$	$\frac{\text{Log } \eta_r \times 10^4}{C}$	$\frac{\text{Log } \eta_r \times 0.75 \times 10^4}{C}$
A. WHOLE RUBBER SOL ^a				
0.004620	1.215	155,000	183,000	137,000
0.01155	1.645	186,000	187,000	140,000
0.04620	7.388	462,000	188,000	141,000
B. PRECIPITATED RUBBER ^b				
0.003278	1.183	186,000	223,000	167,000
0.004214	1.245	194,000	226,000	170,000
0.005900	1.365	206,000	229,000	172,000
0.009833	1.685	232,000	230,000	173,000
0.02950	4.395	384,000	218,000	164,000

^a 1 gram of crepe in 300 cc. of chloroform in a Wolff bottle, kept in darkness 7 days; solution filtered through bolting cloth.

^b Excess methanol, added to solution A, precipitated 43 per cent of rubber in solution; precipitated rubber dried in steam chest in stream of pure nitrogen and redissolved in chloroform.

The viscosity-molecular weight results in Table V for solutions of crepe in chloroform illustrate the effect of using Equations 1 and 2 with Staudinger's K_m and K_{cm} values in comparison with the use of Equation 2 when a K_{cm} value of 0.75×10^4 is employed.

CONCLUSIONS

1. The cryoscopic method is not satisfactory for polyprenes with chain lengths much greater than about 20 isoprene units on account of the failure of their solutions to obey Raoult's law.

2. Since Staudinger's viscosity-molecular weight constants were in many cases determined on nonideal solutions, this subject will be further investigated.

3. The present work has led to the selection of a K_{cm} value of 0.75×10^4 , which is 25 per cent lower than the value chosen by Staudinger, who used higher polymers which do not behave ideally in solution.

4. The use of Staudinger's equation, $M = \eta_{sp}/CK_m$, leads to large deviations with the variations in viscosity usually employed, and this deviation is largely avoided by employing the equation $M = (\log \eta_r/C)K_{cm}$.

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ANALYTICAL METHODS IN RUBBER CHEMISTRY

(IV) THE DETERMINATION OF PEROXIDIC OXYGEN *

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In the previous publication, of Farmer, Tristram and Bolland¹, it was stated that methods were required to estimate the various forms in which oxygen occurs united to the rubber molecule, and a method for the estimation of hydroxyl oxygen was discussed. The determination of peroxidic oxygen in oxidized rubber presents two distinct problems. It is necessary to employ a method which, first, is satisfactory in the presence of unsaturation and, secondly, ensures effective contact between the long rubber chains and the analytical reagent. These requirements are both satisfied by the modification described below of the colorimetric method of Young, Vogt and Nieuwland².

Before describing the modified technique, some mention must be made of the earlier methods and of the errors which arise when they are applied to the determination of peroxidic oxygen in unsaturated compounds. All the earlier methods for the determination of peroxidic oxygen depend on the oxidation of potassium iodide and titration of the liberated iodine. This method is open to the objection that the liberated iodine immediately attacks the double bonds remaining in the oxidized material. This difficulty was recognized by Stephens³, who, using a method in which the peroxidic oxygen was reduced with stannous chloride, succeeded in estimating about 80 per cent of the total peroxide present in cyclohexene peroxide. Yule and Wilson⁴ estimated the peroxide in cracked gasoline by shaking with an acid solution of ferrous thiocyanate and back-titrating the resulting ferric salt with titanous chloride. The results were later contested by Young, Vogt and Nieuwland², who described the colorimetric method which has been adopted, with some modification, in the present work.

The method depends on the estimation of the color developed by ferric thiocyanate in methanol in the presence of sulfuric acid. The procedure for substances soluble in methanol is outlined below. The Duboseq colorimeter used by these workers has been replaced by the Spekker photoelectric absorptiometer (Adam Hilger Ltd., London). A sample of the peroxide is made up to a suitable volume in methanol so that 1 cc. of the solution contains 0.01 to 0.04 mg. of peroxidic oxygen. The reagent is a freshly prepared solution containing 1 gram of ammonium thiocyanate and 1 cc. of 5*N* sulfuric acid in 200 cc. of pure methanol which has been saturated with ferrous ammonium sulfate. One cc. of the peroxide solution is pipetted into 25 cc. of reagent and allowed to stand for 20 mins. The color developed is then compared with the color in the reagent. The instrument is calibrated by measuring the color produced by standard solutions of ferric chloride in methanol. It was found that the calibration curve, using a combination of the light blue (6) and green (5) filters, was linear up to a concentration of 0.05 mg. of peroxidic oxygen in 25 cc. of reagent.

Good results were obtained for certain simple peroxides which were prepared in the pure state, and it has been confirmed that the oxidizing power of the

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peroxide is the same whether it is present as a disubstituted hydrogen peroxide (R.O.O.R) or as a hydroperoxide (R.O.OH).

Additional results were also obtained when hydrocarbons of low molecular weight and containing a similar structure to that of rubber, *viz.*, dihydromyrcene ($C_{10}H_{18}$), dihydrofarnesene ($C_{15}H_{26}$), and squalene ($C_{30}H_{50}$), were oxidized in ultraviolet radiation in the presence of molecular oxygen. It was found, within the experimental errors, that the whole of the oxygen entering into reaction in the very earliest stage combined in the peroxidic form. This fact is a further indication of the validity of the method. A detailed account of this work will be published elsewhere.

The application of the procedure above to the estimation of peroxide in oxidation products of rubber requires the use of a reaction medium in which such substances are soluble. It has been found that a mixture of methanol and benzene (AnalaR) serves the purpose admirably. The actual mixture used in most instances contained 27 per cent by volume of methanol. The choice of composition of the mixture was restricted by the limited solubility of the inorganic reagents in benzene-rich mixtures, and by the insolubility of the organic oxidation products in alcohol-rich mixtures.

TABLE I

Peroxide	Peroxidic oxygen (per cent)	
	Calculated	Observed
Hydrogen peroxide	94.2	89.6
Succinyl peroxide	13.68	13.68; 13.18; 12.88
Dihydroxyheptyl peroxide	12.1	12.1; 12.4
Cyclohexene peroxide	28.1	29.0

In the experimental procedure finally adopted, a measured volume (about 1 cc. containing 0.01 to 0.02 mg. of peroxidic oxygen) of the oxidation product in benzene or cyclohexane solution was diluted to 18 cc. with benzene, and 7 cc. of ferrous thiocyanate reagent, prepared as above in methanol, were added. The intensity of color of the clear liquid obtained by decantation from the precipitated excess of ammonium thiocyanate was determined as before, after a 20-minute interval. It has been shown that the color developed by standard ferric chloride solutions is not at all sensitive to changes in the composition of the solvent mixture in the region employed; in fact, does not differ significantly from that obtained in 100 per cent methanol.

The application of the modified procedure to a few substances soluble both in methanol and a mixture of methanol (27 per cent) and benzene (73 per cent) shows that similar results are obtained in the two media. With the exception of the final example, the samples were solutions of undetermined concentration of crude photooxidation products derived from simple hydrocarbons.

Such comparison is not, of course, possible in the case of rubber derivatives, but in view, first, of their complete solubility in the mixed solvent, together with the fact that development of a coloration is always complete within 20 minutes and, secondly, that in all instances where one procedure can be checked against the other, good agreement has been found, there is every reason to believe that the method is also applicable to this class of substances.

It is not possible to assign any precise order of accuracy to the method when used with rubber derivatives, as no absolute means of checking is available. When the method is used in the determination of homogeneous peroxides, the

error is within the limits of ± 5 per cent of the value determined, and these limits probably apply also to rubber. On the positive side it can be said that, when the method has been applied to solutions of rubber which have absorbed small measured amounts of molecular oxygen, values of peroxide equivalent to 80 per cent of the oxygen intake have been found, in spite of the fact that decay of the peroxide groups in rubber has usually been found to be fairly rapid. This

TABLE II

		Mg. of peroxidic oxygen per cc. of solution	
		MeOH reagent	C ₆ H ₆ -MeOH reagent
Oxidation product from	Sample		
	methylcyclohexene (a).....	0.0185	0.0182
	(b).....	0.0190	0.0186
	(c).....	0.0093	0.0100
	dihydromyrcene	0.0209	0.0204
Dihydroxyheptyl peroxide	cyclohexene	0.0127	0.0123
	0.0127	0.0123

itself points to a lower limit of accuracy which is believed to be greatly below the actual limit.

The above work was carried out as part of the program of fundamental research on rubber undertaken by the Board of British Rubber Producers' Research Association.

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OXIDATION OF UNVULCANIZED RUBBER IN LIGHT *

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When unvulcanized rubber is exposed to light in the presence of air, it develops a tackiness which may proceed far enough to cause partial liquefaction of the rubber. The nature and intensity of the light is unimportant, although the rate is affected. The action is oxidation, and is accompanied in many cases by peroxide formation and a Russell effect.

This production of tackiness under the influence of light is susceptible to the action of organic catalysts, both positive and negative¹. Many materials used regularly as antioxidants in vulcanized rubber are active agents in the development of tackiness. A number of other materials effectively retard the development of tackiness. In many cases they suppress completely the positive action of these commercial antioxidants. Antioxidants appear, therefore, capable of playing a dual role—that of assisting rubber oxidation under some circumstances and that of retarding oxidation under others.

This paper describes a method and apparatus for the quantitative study of the rate of oxidation of raw rubber. In the previous paper¹ the tackiness of the raw rubber was of necessity judged wholly by appearance and feeling. Although it increased with time of exposure to light, in many cases it decreased again after having reached a maximum. We assumed that this subsequent decrease in tackiness was due to additional oxidation, but there was no proof. There was also no evidence that the development of the same degree of tackiness in rubber containing different materials represented the same degree of oxidation.

The oxidation of vulcanized rubber is usually studied by exposure to air or oxygen at elevated temperatures, frequently at increased pressures. The decrease in tensile strength or elongation at break is taken as a measure of the extent of oxidation. There have been attempts^{3, 4, 12} to follow the oxidation of rubber by determining the amount of material soluble in acetone. It is assumed that unoxidized rubber is insoluble and that some of the oxidized rubber is soluble in this solvent. Stevens and Gaunt¹⁰ evaluated the deterioration of latex-impregnated fabric after exposure to light by determining the acetone extract. They found that phenolic materials and primary aryl amines have a protective action. Dufraisse⁵ studied directly the rate of oxidation of vulcanized rubber. He contended that the rate of absorption of oxygen by a sample under given conditions is a truer measure of its probable service life than results obtained by the more common methods. He believed that the method offers practical advantages, since the rate of oxidation may be ascertained in 2 or 3 hours instead of the many days required by some of the conventional accelerated aging tests. Milligan and Shaw⁸ and Morgan and Naunton⁹ studied the absorption of oxygen by vulcanized rubber in a manometric tube.

APPARATUS

The Dufraisse, Milligan and Shaw, and Morgan and Naunton types of apparatus were not believed entirely desirable. Oxidation in the former occurs at a varying pressure.

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The rate of development of tackiness is approximately the same, whether a glass or a fused quartz container is used. On exposure to diffused daylight, the tackiness has the same characteristics but is developed more slowly, owing to the decrease in intensity of the light. It was concluded, therefore, that ultra-violet light was not essential, and that a suitable apparatus could be constructed from glass.

The apparatus (Figure 1) consists of a Pyrex glass tube of 20-mm. bore, closed at one end with a ground-glass stopper. A horizontal tube of 3-mm. bore, about 75 cm. long, was attached to the opposite end. The open end of the small tube was bent at right angles and dipped into a mercury reservoir. The sample was placed in the stoppered tube and exposed to light. As the absorption of oxygen progressed, mercury flowed into the small tube and the distance of flow was measured. The apparatus was always tapped before measurements were made. To convert the readings into cubic centimeters, each tube was calibrated carefully at a number of points with a buret, and calibration curves were drawn. Since changes in the atmospheric pressure affected the readings, a blank tube was always maintained under the same conditions, and its readings were compared with those of the tubes in service. Since the tubes were level, the air in the apparatus was at approximately constant pressure. To obtain a constant temperature, the absorption chamber was enclosed in a box containing a thermostat, an electric bulb, a cooling coil, and a fan. To hold the heat in the box and yet allow light to enter, the top was covered with cellophane. Cellophane is quite transparent, both to visible and ultraviolet light. The samples of rubber were obtained by pressing sheets in a vulcanizing press at 105° C, and were always of the same size. All rubber samples were 1.9×12.7×0.16 cm. and weighed about 3.5 grams. The volume of gas in all tubes was made equal by the insertion of glass strips. To the blank tube was added an additional volume of glass equal to the volume of the sample under test.

In the operation of the apparatus, the samples were placed in the tubes and the box was kept dark, while the temperature was raised about 3° C above that at which the experiment was to be run. When cooled to the temperature of the experiment, the mercury rose into the level portion of the tube. After standing for some time, readings were made of the position of the mercury and the light was turned on. Readings made at suitable intervals were converted into cubic centimeters from the calibration curves. The cubic centimeters absorbed were corrected for changes in the blank tube. Three sample tubes and the blank tube could be operated simultaneously in the apparatus.

It was found that 46° C, was a convenient temperature at which to operate the apparatus. A General Electric S-1 lamp was used as the source of light, and its distance from the samples was 18 inches (46 cm.).

At times it was difficult to check the rate of oxidation of pale crepe, although all samples were taken from the same original lot. The conditions of operation were apparently uniform. It seemed possible that the variation found might be due to a different interval of time elapsing between the milling and pressing into sheets and the determining of the rate of oxidation. Sheets of pale crepe were milled and pressed in the usual manner, and then allowed to stand in the dark at room temperature for various intervals before use. After the sample had stood for 10 days, the rate of oxidation was about twice that of a freshly milled and pressed sheet. As a result, particular attention was given to the elimination of this source of error in all experiments.

OXIDATION RATE

Pale crepe was milled for a short time, sheets were pressed, and samples were exposed to air in the apparatus. The following data are typical of the readings obtained:

Time (hrs.)	Absorption (cc.)	Time (hrs.)	Absorption (cc.)
0.17.....	0.04	3.08.....	0.28
0.58.....	0.05	19.2.....	1.41
1.17.....	0.19	19.5.....	1.44
1.50.....	0.24	25.5.....	1.72
2.58.....	0.20	44.5.....	3.08

These values are plotted in Figure 2. The relation is apparently linear. The line does not go precisely through the origin, presumably on account of initial temperature disturbances due to switching on of the light. The rate of absorption

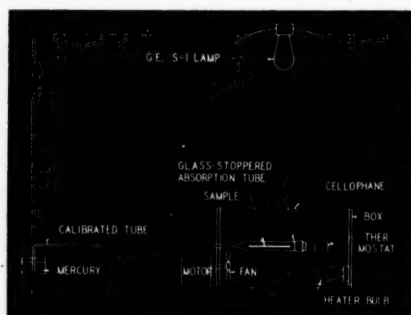


FIG. 1.—Apparatus for study of oxidation.

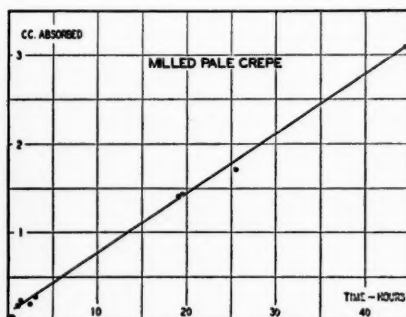


FIG. 2.—Data on milled pale crepe.

may be expressed by the slope of the line, given in cubic centimeters absorbed per hour for the specific size of sample used. The values obtained for three determinations on pale crepe are as follows:

Pale crepe No.	Absorption rate at 46° C (cc. per hr.)
1.....	0.069
2.....	0.069
3.....	0.062
Average	0.067

Retarders.—In the previous paper,¹ sulfur, benzidine, and hydroquinone were found to be effective agents in preventing the development of tackiness. Two per cent of each of these materials was milled into pale crepe, and the rate of oxidation of the mixture determined. The results are as follows:

Added material	Absorption rate at 46° C (cc. per hr.)
None	0.067
2 per cent sulfur.....	0.028
2 per cent benzidine.....	0.014
2 per cent hydroquinone.....	0.014

It is evident that these materials retard appreciably the rate of oxidation of raw rubber in light.

Antioxidants.—It was found previously that some ordinary antioxidants accelerate the development of tackiness. Two per cent of each of four antioxidants was milled into pale crepe and the rate of oxidation determined:

Added material	Absorption rate at 46° C (cc. per hr.)
None	0.067
2 per cent phenyl- β -naphthylamine (Agerite Powder).....	0.076
2 per cent di- β -naphthyl- <i>p</i> -phenylenediamine (Agerite White) ..	0.043
2 per cent trimethyldihydroquinoline (Agerite Resin D).....	0.062
2 per cent phenylphenol (Parazone).....	0.050

Although each of the rubber samples was much more tacky than the blank, the rate of oxygen absorption by these antioxidant-containing samples was not uniformly higher than that of the blank.

Percentage of antioxidant.—A series of samples was prepared containing different percentages of Agerite Powder, and their rates of oxidation were determined with the following results:

Agerite Powder (percentage)	Absorption rate at 46° C (cc. per hr.)
None	0.067
0.5	0.090
1	0.076
2	0.076
4	0.071

This addition of 0.5 per cent of the antioxidant raises the absorption rate materially. The addition of further quantities decrease the rate of absorption. This is contrary to the implication of the physical appearance of the samples. The tackiness developed was progressively greater with an increasing amount of antioxidant.

Agerite Powder is soluble in raw rubber at room temperature to the extent of about 1 per cent. A mixture of less than this amount gives a clear transparent rubber, while the addition of greater amounts produces an increasingly opaque material. It was thought possible that the exposure of an opaque rubber to light might give an appreciably lower rate of oxygen absorption, since the light would tend to affect the surface only. In such a case oxidation might occur primarily at the surface rather than throughout the mass, as in a transparent material. This would give a lower over-all absorption, but would not affect the development of tackiness.

Effect of Fillers.—Portions of various fillers were added to pale crepe to make it opaque. Sheets were pressed and the rates of oxygen absorption were determined. The relation in each case was a straight line. The constants were calculated to be as follows:

Per cent	Material	Cc. per hr.
Blank	Pale crepe	0.067
5	Titanium dioxide	0.020
2	Zinc oxide	0.020
5	Zinc oxide	0.010
5	Whiting	0.036
1	P-33 carbon black.....	0.018

The addition of a small amount (2 per cent) of zinc oxide decreases the absorption rate to about one-third of the value for transparent pale crepe. The addition of more zinc oxide reduces this value still further. The addition of either 5 per cent titanium dioxide or 1 per cent P-33 carbon black reduces the absorption of pale crepe also to one-third of its original value. The addition of 5 per cent whiting reduces the absorption appreciably, but it is not so effective, since it does not give so opaque a composition as do the other fillers.

These results suggest a possible explanation of the anomalous data obtained with the various antioxidants. Their addition to rubber increases the development of surface tackiness in each case. They may be insoluble in rubber, however, and give an opaque mixture whose total absorption of oxygen is relatively low.

Effect of Fillers and Antioxidants.—Samples of pale crepe containing Agerite White and Agerite Powder, respectively, were mixed with fillers and exposed to light in the presence of air. The rates of oxidation follow:

Antioxidant	Filler	Cc. per hr.
—	—	0.067
—	2 per cent zinc oxide	0.020
2 per cent Agerite White	—	0.043
2 per cent Agerite White	2 per cent zinc oxide	0.037
2 per cent Agerite Powder	—	0.076
—	2 per cent titanium dioxide	0.020
2 per cent Agerite Powder	2 per cent titanium dioxide	0.055

The addition of the filler to the sample of crepe containing the antioxidant gave a lower rate of absorption than that containing no filler. On the other hand, the sample of rubber containing both antioxidant and filler had an appreciably higher rate of absorption than that containing the filler alone. By the use of a filler to give a constant degree of opaqueness, the antioxidant definitely accelerated the oxidation of the pale crepe when exposed to light.

Effect of Fillers and Retarding Agents.—Samples of pale crepe were mixed with 2 per cent hydroquinone and 2 per cent sulfur, respectively, and 5 per cent titanium dioxide was added to each. Their rates of absorption follow:

Added material	Filler	Cc. per hr.
—	—	0.067
—	5 per cent titanium dioxide	0.020
2 per cent sulfur	—	0.028
2 per cent sulfur	5 per cent titanium dioxide	0.009
2 per cent hydroquinone	—	0.014
2 per cent hydroquinone	5 per cent titanium dioxide	0.009

The addition of titanium dioxide to give constant opaqueness demonstrates the effectiveness of hydroquinone and sulfur as reagents for the reduction of the rate of oxidation of pale crepe in the presence of light.

Effect of Oxidation Accelerators.—Benzoyl peroxide is well known as an oxidizing agent for organic materials. RPA-2 is assumed to be an oxidation catalyst for rubber, since it increases materially the rate of breakdown of rubber during milling. The rate of oxidation of samples containing 2 per cent of each of these materials was determined:

Added material	Absorption rate at 46° C (cc. per hr.)
None	0.067
Benzoyl peroxide	0.305
RPA-2	0.163

These samples both became very tacky in a short time, which is consistent with the greatly increased rate of oxidation.

Effect of Vulcanization Accelerators.—As a test of the influence of accelerators on the rate of oxidation, samples of rubber were mixed with mercaptobenzothiazole and with diphenylguanidine. These materials displayed a slightly reduced rate of oxidation, compared with the appropriate blanks.

Effect of Temperature and Light.—By the addition of a resistance coil heater, it was possible to operate the apparatus at 66° C. At this temperature the oxidation of raw rubber proceeds at a sufficiently rapid rate to allow determinations, both in the light and in the dark which was impractical at 46° C.

Samples of pale crepe containing sulfur, benzidine, or hydroquinone had practically the same rate of oxidation in the light as in the dark. A blank pale crepe sample oxidized about four times as rapidly in the light as in the dark. Pale crepe containing Agerite Powder oxidized about six times as fast in light as in darkness, at this temperature.

Effect of oxygen.—All of the experiments above were in air. It might be expected that, since air contains only about 20 per cent oxygen, the use of pure oxygen would increase the rate of oxidation five times. A series of determinations was made in oxygen. These values and those for the corresponding rate in air follow:

Added material	Rate at 46° C (cc. per hr.)	
	Air	Oxygen
2 per cent Agerite Powder.....	0.076	0.095
2 per cent Agerite White.....	0.043	0.064
2 per cent titanium dioxide.....	0.020	0.039

The use of oxygen does increase the rate somewhat, but the increase is relatively small. We may conclude that the rate of oxidation is not proportional to the partial pressure of oxygen. This is somewhat similar to the conclusion of Williams and Neal¹¹ and Morgan and Naunton⁹, who showed that the rate of oxidation was independent of the partial pressure, provided the size of the sample was such that the oxygen could diffuse through the rubber with sufficient rapidity.

RUBBER SOLUTIONS

Solutions of rubber decrease in viscosity when exposed to light; this action is probably a manifestation of oxidation. It was thought that this process might parallel the development of tackiness in light, and that it might be accelerated and retarded by the same reagents.

A lot of clear rubber solution was prepared by the diffusion of smoked sheets into benzene. The solution contained 5.5 per cent rubber. It was divided into three portions: One was a blank, to the second was added 2 per cent of Agerite Powder on the rubber, and to the third, 2 per cent of benzidine.

The viscosity of each of these solutions was determined in a Stormer viscometer at 27° C, using a 600-gram weight in place of the usual 100-gram weight. The solutions were then exposed in glass bottles to the S-1 lamp for 18 hours at a distance of 18 inches. The viscosities were again measured with the following results:

Added material	Viscosity (min.)	
	Original	After exposure
None	2.82	0.41
Agerite Powder	2.96	0.085
Benzidine	2.80	1.62

It is evident that Agerite Powder, an activator of tackiness development, also accelerates the decrease in viscosity in light, whereas benzidine acts as a retarder in both cases.

DISCUSSION

The qualitative results on the oxygen absorption of uncured rubber, as reported previously, have been confirmed by quantitative measurements. Many of the common commercial antioxidants are active accelerators of this type of oxidation. Others materials, such as sulfur, benzidine, and hydroquinone, retard this type of oxidation appreciably and may be regarded as protective agents against it. Transparent raw rubber oxidizes at an appreciably higher rate in the presence of light than an opaque rubber.

There is some disagreement between figures^{2, 6, 7} on the amount of oxygen necessary to deteriorate vulcanized rubber, but it may be concluded that the absorption of roughly 1.0 per cent results in its complete destruction. The amount of oxygen involved in our results may be calculated; 3.5 grams of raw rubber are made tacky by the absorption of 3 cc. of oxygen. This corresponds, under the above conditions, to about 0.05 per cent. This amount is only a small fraction of that needed to destroy vulcanized rubber. On the other hand, there is considerable evidence that tacky raw rubber is far from being useless when vulcanized. Lower tensile-strength values are obtained, but they may be only moderately lower than those obtained on normal rubber.

According to our data, the oxidation of raw rubber in light seems to be a linear function of time. Evidence in the literature^{9, 11} implies this straight-line relation, although Kohman⁶ found an S-shaped curve, suggesting an auto-catalytic reaction. A linear relation gives the appearance of a zero-order reaction. This would suggest that the rate is independent of the concentration of oxygen. There is much evidence indicating that the rate of oxidation increases but slightly with an increase in oxygen concentration. Under many experimental conditions, the rate of oxygen diffusion is the controlling factor. When oxidation is slow, either as a result of low temperatures or of the retarding effect of catalysts, the rate of diffusion is not the controlling factor. It is probable that, under these conditions, the rate of oxidation is unaffected by the oxygen concentration. The chain theory of oxidation is probably consistent with a zero-order reaction, and there are theories of the action of antioxidants on this basis. Some of these theories involve the presence of peroxides. It was indicated in the previous paper, however, that peroxide formation, as determined by the Russell effect, was frequently associated with acetone-soluble material and not necessarily with the rubber hydrocarbon.

It is well demonstrated that commercial antioxidants do retard the oxidation of vulcanized rubber in the dark. On the other hand, we have shown that these same materials are accelerators of the oxidation of raw rubber in light. Any satisfactory theory of the oxidation of rubber and of the function of antioxidants must take into account this anomalous behavior of these materials.

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A MANOMETRIC TEST FOR OXYGEN ABSORPTION BY VULCANIZED RUBBER *

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The object of this work was: (1) to set up in laboratory glassware an apparatus which might confirm the results obtained by Dufraisse in his manometric test¹ for oxygen absorption in metal apparatus; (2) to study the relative tendencies of different rubber compounds to absorb oxygen; (3) to determine the relationship between the rates of oxygen absorption of rubber compounds by the modified Dufraisse method and their rates of tensile-strength deterioration in the oxygen bomb.

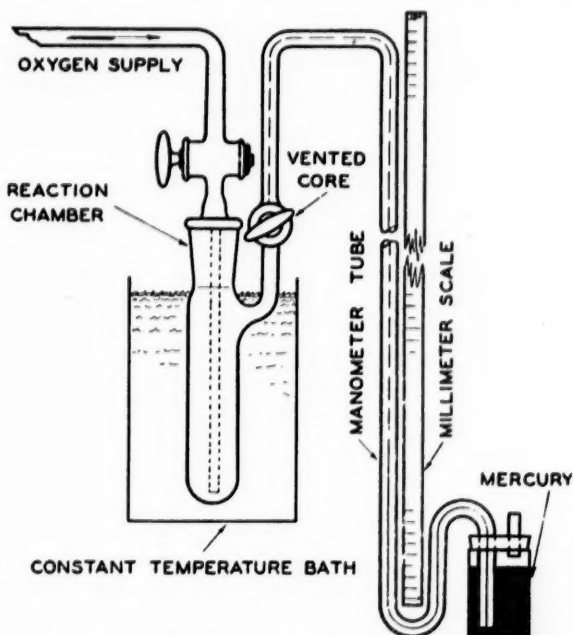


FIG. 1.—Schematic arrangement of oxygen absorption apparatus.

APPARATUS

The apparatus (Figure 1) consists of one or more sealed glass reaction chambers which contain the samples in an atmosphere of oxygen, and are immersed in an oil bath maintained at 100° C. A mercury manometer tube with a millimeter scale is attached to each reaction chamber to permit measurement of the reduction of pressure.

The reaction chambers are made of heavy-walled Pyrex glass. The outside dimensions are 3.5 inches in height by 0.875 inch in diameter. The capacity is about 25 cubic centimeters. Each chamber is sealed with a tapered, well greased, ground-glass stopper.

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Passing through the center of this stopper is a length of small-diameter glass tubing, which reaches to the bottom of the reaction chamber, allowing the oxygen to be introduced there. At the top of the reaction chamber there is a side-arm with a three-way stopcock, so that the air and oxygen used in flushing out the chamber may be vented through its core. To this side-arm is connected the manometer tube.

COMPOUNDS USED IN OXYGEN ABSORPTION TESTS

	A	B	C	E
Smoked sheet	100	100	100	100
Stearic acid	1	1	1	1
Zinc oxide	56	56	56	56
Gilder's whiting	54	54	54	54
Agerite-White	—	—	—	1
Agerite-Resin-D	—	1	—	—
Sulfur	3	3	1	—
Altax (Benzothiazyl disulfide).....	1	1	1	—
Zimate (Zinc methylxanthate).....	0.1	0.1	—	—
Tuads (Tetramethylthiuram disulfide)...	—	—	0.3	3
Telloy (Tellurium)	—	—	—	0.5
Curing temperature	287° F	287° F	258° F	274° F

TENSILE PROPERTIES

Stress at 300% (S)—Tensile (T)—% Elongation at Break (E)
Before Aging

Press cures of slabs	A			B			C			E		
	S	T	E	S	T	E	S	T	E	S	T	E
10 minutes	Uncured			Uncured			—	—	—	—	—	—
15 minutes	—	—	—	—	—	—	—	—	—	475	2180	620
20 minutes	890	2680	600	860	2650	580	Uncured			—	—	—
30 minutes	780	2500	600	740	2600	600	Slightly Cured			710	2560	560
40 minutes	—	—	—	—	—	—	870	2640	560	—	—	—
45 minutes	710	2350	610	700	2370	600	—	—	—	790	2600	540
50 minutes	—	—	—	—	—	—	850	2640	520	—	—	—
60 minutes	720	1960	570	715	2065	590	845	2355	500	790	2540	520

After Aging in Oxygen Bomb (70° C and 300 lbs. oxygen)

Cure (° F)	30 min. at 287°			30 min. at 287°			40 min. at 258°			45 min. at 274°		
	S	T	E	S	T	E	S	T	E	S	T	E
2 days of aging...	770	2030	540	905	2290	540	850	2550	520	735	2280	520
4 days of aging...	700	1735	530	985	1950	510	815	2500	525	765	2250	525
7 days of aging...	720	1530	500	900	1840	490	890	2350	500	870	2220	500
14 days of aging...	—	535	220	880	1140	380	850	1980	500	850	2040	490
21 days of aging...	—	Melted	—	—	730	280	810	1810	490	850	1980	480
28 days of aging...	—	—	—	—	650	230	610	1230	490	730	1640	480

Note: The oxygen bomb aging data shown above were taken from *Vanderbilt News*, 11, No. 2, 5 (1941).

PROCEDURE

Die out as many T-50 pieces from each slab of rubber compound to be tested as may readily be accommodated by one reaction chamber, and weigh. Stand these pieces upright, side by side in the reaction chamber. Grease all the stopcocks and all the ground-glass fittings with a good grade of white petrolatum to prevent leakage. Now immerse the reaction chambers containing the samples in the constant-temperature oil bath, and connect them with the oxygen supply. Allow a slow current of oxygen to pass through for ten minutes to be sure the inside atmosphere consists of oxygen alone. Now stop the flow of oxygen and immediately close all the stopcocks on the reaction chambers.

Connect the manometer tubes to the side-arms of the reaction chambers, and open the stopcocks to the manometer tubes. As the temperature within the reaction chamber rises, the mercury level in the manometer tubes will be depressed until the final temperature of 100°C is reached throughout. Open the vent cock on each chamber to the room to reduce the pressure within the reaction chambers to atmospheric. This will cause a rise in the height of the columns of mercury.

The readings at this point are taken as the zero points. Readings of the millimeter scale are taken each five minutes during the first hour and each fifteen minutes during the second hour. At the end of two hours, enough readings have been taken to define the relative rates at which the rubber compounds absorb oxygen.

DISCUSSION OF PROCEDURE

The rate of oxidation of a sample of given volume is a function of the surface area of that sample. Theoretically, the smaller the particles of a finely divided sample, the faster the oxidation. If the particles are too fine, however, too many of the surfaces will touch and will, therefore, not have good oxygen contact. Also there will be air trapped between the particles that will not be replaced by oxygen. Conversely, if the particles are too large, the surface area per volume will be too small for speedy results.

After several trial runs with samples prepared in various ways, T-50 specimens were chosen as the best type of sample, because they seemed to give the most favorable surface-volume ratio. T-50 pieces totaling 6.6 grams also gave a suitable ratio of volume of sample to volume of reaction chamber to produce reasonably quick and accurate results. All succeeding tests were run with this weight of sample. Each of the four compounds used in this test had the same specific gravity and therefore each sample had the same volume. Since die-cut specimens were used, each sample had not only the same volume but the same surface area.

COMPOUNDS USED

The compounds used in this oxygen absorption tests were the same as four of the five used by the Vanderbilt Laboratory in correlating oxygen-bomb aging at 70°C and at 80°C .

Duplicate determinations of Compound A, cured 30 minutes, were run simultaneously in separate chambers. Duplicate determinations on Compound A, cured 45 minutes, were made in the same manner. The splendid check results show that one reaction chamber duplicated the other.

Similarly, duplicate determinations on Compound B, cured 60 minutes, were run five days apart. The excellent check results show that a test made one day could be duplicated later.

The accompanying graphs show the curves for the rate of oxygen absorption for the various cures by the four compounds listed above.

DISCUSSION OF THE GRAPHS

Graph No. 1 shows the rate of oxygen absorption by Compound A, cured 20, 30, 45 and 60 minutes at 287°F . Graph No. 2 shows the same for Compound B. Compound B is the same as A plus 1 part of Agerite Resin D. The results definitely show the advantage of an antioxidant in the compound for slowing the

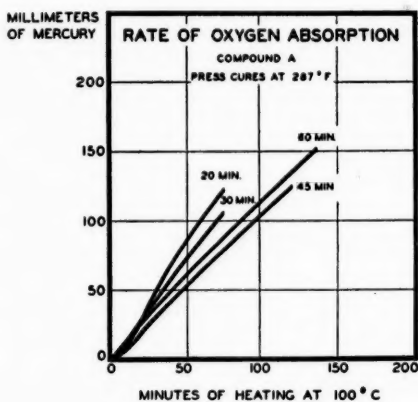
HEIGHT OF MERCURY COLUMN IN MILLIMETERS DURING TEST

Curing temp. Time of heating of samples at 100° C	A 287° F						B 287° F						C 258° F						E 274° F																												
	30'			45'			20'			30'			45'			30'			40'			50'			60'			15'			30'			45'			60'										
	Millimeters						Millimeters						Millimeters						Millimeters						Millimeters						Millimeters						Millimeters						Millimeters				
0 minutes	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0													
5 minutes	4	5	7	2	1	6	5	2	1	1	3	2	1	1	3	0	1	1	3	4	6	1	3	4	7	1	1	1	1	1	1	1	1	1	1												
10 minutes	10	11	12	6	5	12	9	4	3	4	6	13	6	5	7	9	10	13	14	14	19	21	21	24	26	27	27	27	27	27	27	27	27	27	27												
15 minutes	18	20	21	12	11	18	16	8	8	10	12	13	14	14	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16												
20 minutes	26	28	27	18	17	24	17	10	10	13	14	14	14	14	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16												
25 minutes	40	37	36	24	22	30	21	14	13	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16												
30 minutes	48	42	42	29	27	36	21	14	13	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16												
35 minutes	57	48	48	35	32	42	23	17	15	18	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19												
40 minutes	66	56	56	41	38	48	27	21	16	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21												
45 minutes	76	64	63	45	43	53	32	24	18	23	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24												
50 minutes	85	71	71	50	48	58	35	25	20	26	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27												
55 minutes	92	79	79	56	54	65	37	28	23	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30												
60 minutes	100	86	85	62	60	70	42	32	26	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32												
75 minutes	123	106	105	79	77	85	52	42	34	39	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40												
90 minutes	—	—	—	95	91	—	58	49	42	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47												
105 minutes	—	—	—	—	—	—	66	58	47	54	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53	53												
120 minutes	—	—	—	111	107	—	76	66	53	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60												
135 minutes	—	—	—	127	124	—	84	72	60	67	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66	66												
150 minutes	—	—	—	—	—	151	94	83	65	73	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72												
165 minutes	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—												
180 minutes	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—												

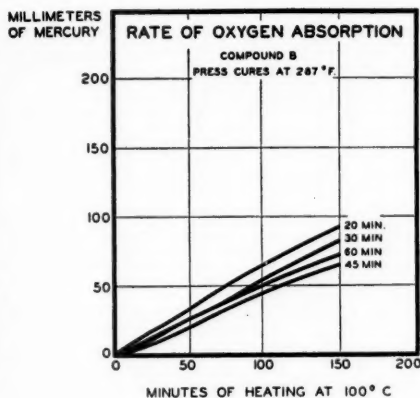
Slightly cured

rate of oxygen absorption. This observation correlates favorably with tensile-strength deterioration data obtained from oxygen-bomb aging.

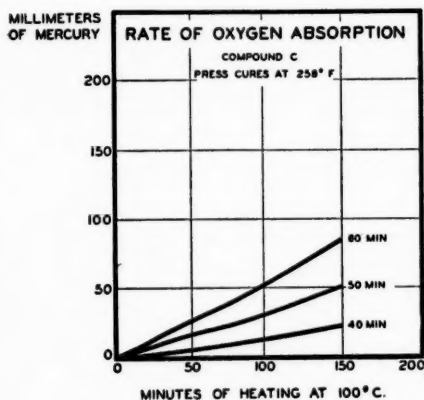
The curves for the various cures of Compounds A and B fall in the same relative positions. The 20-minute cures have the highest rate of absorption. The 45-minute cures have the lowest rate of absorption. The 30- and 60-minute cures fall between the 20- and 45-minute cures, with the 60-minute cures lower than the 30-minute cures.



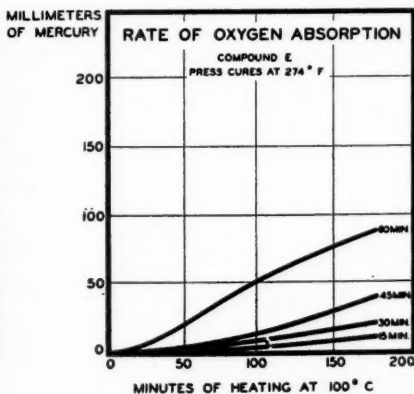
GRAPH No. 1.



GRAPH No. 2.



GRAPH No. 3.



GRAPH No. 4.

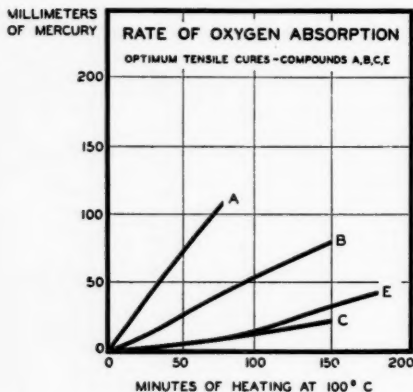
From the standpoint of oxygen absorption alone, the 45-minute cures for Compounds A and B are the best. These are past the optimum cure with respect to the tensile strength of the unaged compounds.

Graph No. 3 shows the rate of oxygen absorption by Compound C cured 40, 50 and 60 minutes at 258° F. This compound contains low sulfur, with no antioxidant, on the standard base. Compound C, however, is vulcanized at a lower temperature than A and B, *i.e.*, at 258° F instead of 287° F. This compound has a much lower rate of oxygen absorption than either A or B, especially

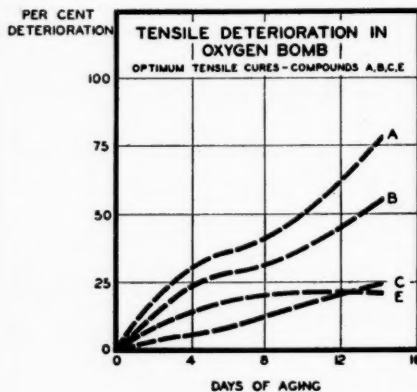
at the 40-minute cure. Compound C also has a lower rate of tensile strength deterioration in the oxygen bomb than Compounds A and B.

Judging from the rate of oxygen absorption, the 40-minute cure is the best. This cure also is the optimum cure with respect to the tensile strength of the unaged compound.

Graph No. 4 shows the rate of absorption by Compound E, cured 15, 30, 45 and 60 minutes at 274° F. This compound is the standard base compound, with one part of an antioxidant, but with no sulfur. It is vulcanized with Tuads and Telloy. This compound has a much lower rate of oxygen absorption than either A or B. Considering all the cures of Compound C and E, Compound E has a lower rate of absorption than Compound C. However, in looking at the specific cures used in the oxygen bomb study, *i.e.*, 40 minutes at 258° F for Compound C and 45 minutes at 274° F and E, Compound C absorbs oxygen slower than E. The same comparison is seen in the tensile-strength deterioration data for the first seven days of aging in the oxygen bomb.



GRAPH No. 5.



GRAPH No. 6.

In the case of Compound E the shortest cure has the lowest rate of oxygen absorption, with the longer cures having progressively higher rates of absorption.

Graph No. 5 shows the rate of oxygen absorption by the optimum tensile cures of the four compounds. The normal sulfur compound with normal acceleration, Compound A, has the highest rate of oxygen absorption. Compound B, with normal sulfur and acceleration plus one part of an antioxidant, is next highest. The low-sulfur compound, C, has the lowest rate of oxygen absorption. The sulfurless compound, E, has a slightly higher rate of oxygen absorption than C.

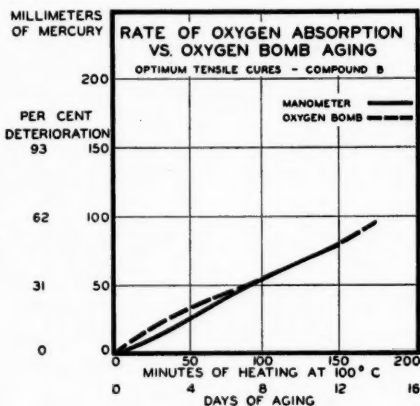
Graph No. 6 shows the rate of tensile-strength deterioration at the optimum tensile cures of the four compounds when aged in the oxygen bomb. These curves are plotted somewhat unusually, in that 100 per cent deterioration is shown at the top of the vertical axis and 0 per cent deterioration at the bottom. This upside-down method causes these curves to take the same general direction as the oxygen absorption curves. The curves for the individual compounds have the same relative positions, whether compared by the manometric method or by the oxygen-bomb aging method.

Graph No. 7 shows, plotted in the solid line, the rate of oxygen absorption by the optimum tensile cure of Compound B. The broken line shows the rate of

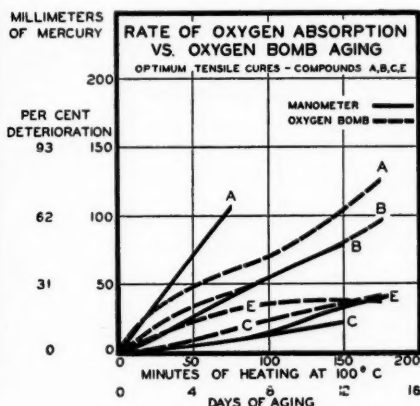
tensile-strength deterioration of the same compound and cure when the point of 50 per cent deterioration is purposely made to coincide with the height in millimeters of the mercury column after heating for 150 minutes. Thus the two curves practically coincide.

Graph No. 8 shows, plotted in solid lines, the rate of oxygen absorption by the optimum tensile cures of the four compounds. The dotted lines show the rate of tensile-strength deterioration of the compounds in the oxygen bomb when the point of 50 per cent deterioration of Compound B is made to coincide with the height in millimeters of the mercury column of the same compound after heating for 150 minutes. Thus when the curves for the rate of deterioration of the compounds in the oxygen bomb are so plotted on the ordinates of the oxygen absorption graph that the two curves for Compound B coincide as nearly as possible, the other curves all fall in the same relative positions.

Furthermore, the curves for the rate of oxygen absorption are spread out more fanwise than are the tensile-strength deterioration curves. Thus when



GRAPH No. 7.



GRAPH No. 8.

results are plotted on comparable ordinates, the differences in the aging characteristics of these four compounds show up to a greater degree by the oxygen absorption method than by the oxygen bomb method.

SUMMARY

An apparatus can be set up in laboratory glassware that will confirm the results obtained by Dufraisse in his manometric test for oxygen absorption. It has been shown that different rubber compounds possess different tendencies to absorb oxygen. It has also been shown that the differences in the rate at which rubber compounds absorb oxygen are comparable with those differences found in the rate of tensile-strength deterioration of the same compounds aged in the oxygen bomb.

This modified Dufraisse manometric method is convenient, efficient, accurate and, above all, a speedy method for measuring the relative aging behavior of vulcanized rubber compounds. Within two hours it is possible to have the results by this method, whereas it is necessary to wait from four days to two weeks for such information by the oxygen bomb method.

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STUDIES IN THE STEROL GROUP

PART XLIII. THE UNSAPONIFIABLE PORTION OF THE ACETONE EXTRACT OF PLANTATION RUBBER *

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The raw material of the present investigation was the acetone extract of 100 pounds of plantation crepe rubber. On concentration, this deposited a few grams of sparingly soluble material consisting of quebrachitol, sterol glucoside, and nitrogenous and phosphatic substances. The unsaponifiable portion, isolated by the usual methods, yielded, on treatment with alcohol, a crystalline solid and a mother liquor from which a reddish gum was obtained.

The solid fraction, after repeated crystallization, had the m. p. 135.5° (Whitby, Dolid, and Yorston¹ give m. p.'s 133-134°, 134-135°, and 125° for various preparations), and was characterized readily by the preparation of acetyl, benzoyl, and *p*-nitrobenzoyl derivatives. Analytical evidence suggested the composition C₂₉H₅₀O; this was confirmed by quantitative hydrolysis of the acetate and by a molecular weight determination based on *x*-ray data, for which we are indebted to Miss D. Crowfoot. Titration with perbenzoic acid indicated the presence in the molecule of one double bond, and the isolation of a substance indistinguishable from stigmastanyl acetate on catalytic hydrogenation of the acetate revealed that the material belonged to the phytosterol group. Further evidence of this association was forthcoming from a selenium dehydrogenation carried out at a high temperature, hydrocarbons similar to those obtained from sterols under like conditions² being obtained. These included a *chrysene*, m. p. 172-173°, and a *picene*, m. p. 274-276°, their respective structures being deduced from their absorption spectra, which are closely analogous to those described by Mayneord and Roe³ for chrysene and picene. In addition, there was isolated a *hydrocarbon*, m. p. 227° (2,7-dinitroanthraquinone derivative, m. p. 242-243°), which, although quite similar to, is not identical with, either of the hydrocarbons obtained by Ruzicka *et al.*² from phytosterols.

Despite the apparent homogeneity of the sterol as outlined above, chromatographic analysis demonstrated that it was actually a mixture, although a pure component could not be obtained by this means. This was also suggested by *x*-ray diffraction photographs, which showed a very close relationship with certain phytosterol mixtures (private communication from Miss D. Crowfoot). A more effective resolution was obtained by repeated fractional crystallization of the acetate, which resulted in the separation of two distinct components. For convenience the corresponding sterols will be referred to as sterols A and B, and their physical constants, together with those of the corresponding acetyl and benzoyl derivatives, are summarized in the accompanying table with similar data for β -sitosterol⁴.

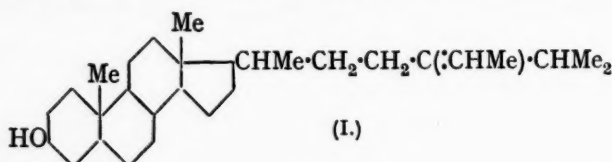
	Sterol		Acetyl derivative		Benzoyl derivative	
	M. p.	$[\alpha]_D^{20}$	M. p.	$[\alpha]_D^{20}$	M. p.	$[\alpha]_D^{20}$
β -Sitosterol	136-137°	— 37°	125-126°	— 41°	146-147°	— 13.8°
Sterol A	135.5	— 37	123.5	— 41	147	— 15.2
Sterol B	134	— 26	114-116	— 28	145	— 14.9

* Reprinted from the *Journal of the Chemical Society*, June 1941, pages 344-347.

The results recorded above indicate that sterol A is identical with β -sitosterol, and no depression in melting point was observed on admixture with authentic material from wheat germ oil. Further, catalytic hydrogenation of sterol A gave stigmastanol indistinguishable from specimens obtained by the authors by the complete hydrogenation of fucosterol⁵.

	Alcohol		Acetyl derivative		Phenylurethane	
	M. p.	$[\alpha]_D^{20}$	M. p.	$[\alpha]_D^{20}$	M. p.	$[\alpha]_D^{20}$
Stigmastanol	133°	+ 23°	128.5-129.5°	+ 13.0°	169-170°	+ 13.8°
Dihydro-sterol A . . .	133-133.5	+ 23	128 -128.5	+ 11.5	169-170	+ 13.9
Dihydro-sterol B . . .	126.5	+ 5.8	122 -123	- 8.2		

Sterol B, composing rather less than 10 per cent of the original sterol mixture, on titration with perbenzoic acid, gave a value corresponding to one ethenoid linkage, and on ozonolysis of the acetate, acetaldehyde was obtained in 22 per cent yield (estimated as the 2,4-dinitrophenylhydrazone), indicating the presence of an ethylidene group in the side chain, and suggesting the constitution (I) for this sterol. Only a trace of formaldehyde and no acetaldehyde could be detected on ozonolysis of the hydrogenation product of the acetyl derivative of sterol B.



The latter is not, however, identical with stigmastanyl acetate (see table), a fact which is not entirely unexpected, since reduction of the ethenoid linkage involves the introduction of an asymmetric centre at C₂₄. In this connection, it might be noted that campesterol⁶ differs from 22, 23-dihydrobrassicasterol only in the optical configuration about C₂₄. We would emphasize that sterol B has not yet been obtained completely free from β -sitosterol, since a small quantity of an α,β -unsaturated ketone was isolated from the product of oxidation by the Oppenauer method. Limited by the availability of material, attempts to isolate in a pure condition the 24,28-dehydrostigmastanol (I), which is almost certainly the major component of the sterol B complex, have been unsuccessful and, as it is impossible meantime to continue this work, it has been decided to place the results on record. It has recently been demonstrated that the unsaturated side chains of brassicasterol⁷ and α -spinasterol⁶ are identical with those of ergosterol and stigmasterol, respectively, and that the side chain of zymosterol contains an isopropylidene group.⁸ The suggestion that the nonsaponifiable portion of the acetone extract of rubber contains a sterol, in which an ethylidene group is located in the side chain, is of interest in that it points to the existence of yet another type of unsaturated side chain in naturally occurring sterols.

When the reddish gum from the original mother liquor was distilled in a high vacuum (10^{-3} mm.), a colorless waxy substance passed over at 80-90° C. This was readily purified, and its constants together with those of the acetyl derivative and phenylurethane prove it to be eicosyl alcohol and not octadecyl alcohol, as suggested by Bruson, Sebrell, and Vogt⁹, who actually call attention to the fact that their octadecyl alcohol depressed slightly the melting point of an authentic specimen. The crystalline distillate obtained at 120-130° C is probably steroid

in nature. Above this temperature extensive decomposition occurred, and the small quantity of viscous oil which distilled contained ketonic material, part of which was identified by the preparation of a 2,4-dinitrophenylhydrazone giving the analysis required for the derivative of a steroid ketone. The remainder of the ketonic fraction yielded a complex dinitrophenylhydrazone which could not be resolved; that this is a product of pyrolytic decomposition was revealed by the fact that treatment of the original gum with the Girard reagent P failed to reveal the presence of any ketonic substance. Since high-vacuum distillation yielded no satisfactory separation, attention was directed to the removal of hydroxylic compounds from the original gum by means of the acid succinates, but this only resulted in the isolation of a further quantity of the sterol mixture and eicosyl alcohol. Careful fractionation of the nonhydroxylic residue, both by distillation in a high vacuum and by solvent treatment, failed to yield any tractable material. Examination of the acetone extract of crepe rubber twelve months older than that employed in the above investigation revealed an even lower proportion of volatile nonhydroxylic substances.

EXPERIMENTAL

All rotations were carried out in chloroform solution in a 1 dm. tube. The melting points are uncorrected.

The crude acetone extract from crepe rubber (100 pounds), concentrated to 2.5 liters, was filtered and evaporated to dryness under reduced pressure. The residue (1100 grams) was shaken for 72 hours with methyl-alcoholic potassium hydroxide (5 liters; 5 per cent), the alcohol removed under reduced pressure, and the residue extracted with ether. Washing the extract with water yielded a deep red, voluminous aqueous phase and a yellow ethereal phase which contained the bulk of the unsaponifiable substances. A considerable further quantity of the latter, however, was obtained by reextracting the aqueous phase with much ether. The total unsaponifiable fraction (210 grams) in hot alcohol (4 liters) was decanted from a small amount of tarry substance and cooled; the crude sterol (85 grams) then separated. Removal of solvent from the mother liquor under diminished pressure yielded an oily red gum.

The sterol mixture.—The crude sterol, purified by several recrystallizations from alcohol, formed colorless plates, m. p. 133.5° [= (perbenzoic acid), 0.97 (Found: C, 82.7; H, 12.0. Calc. for $C_{29}H_{50}O, \frac{1}{2}C_2H_5 \cdot OH$: C, 82.3; H, 12.2%). (The presence of alcohol of crystallization is confirmed by the x-ray investigations made by Miss D. Crowfoot.) Acetate: needles from alcohol, m. p. 123.5° [Found: C, 81.7; H, 11.5; *M* (by hydrolysis of acetate), 456, 457, 455. Calc. for $C_{31}H_{52}O_2$: C, 81.5; H, 11.6%; *M*, 456]. Benzoate: plates from alcohol, m. p. 147.5° (Found: C, 83.4; H, 10.6. Calc. for $C_{36}H_{54}O_2$: C, 83.3; H, 10.5%). *p*-Nitrobenzoate: pale yellow microneedles from alcohol, m. p. $183-184^{\circ}$ (Found: C, 76.8; H, 9.6. Calc. for $C_{36}H_{53}O_4N$: C, 76.7; H, 9.5%). Dihydro derivative of acetate (by reduction of acetate in the presence of Adams catalyst at room temperature and pressure): plates from acetone, m. p. 130.5° , $[\alpha]_D^{20} + 14.3^{\circ}$ (*c*, 2.0) (Found: C, 81.4; H, 11.7. Calc. for $C_{31}H_{54}O_2$: C, 81.1; H, 11.9%). The dihydrosterol obtained by alkaline hydrolysis of the dihydroacetate formed plates from acetone, m. p. $134.5-135.5^{\circ}$, $[\alpha]_D^{20} + 24^{\circ}$ (*c*, 1.8), and gave a slight Liebermann-Burchard test (Found: C, 83.7; H, 12.7. Calc. for $C_{29}H_{52}O$: C, 83.6; H, 12.6%).

Selenium dehydrogenation of the sterol mixture.—The dry mixed sterol (35 grams) was heated with dry selenium (60 grams) in a nitrite bath, the

temperature of which varied between 320° and 400° during 72 hours. The pulverized product was extracted (Soxhlet) first with ether and then with benzene. Traces of phenolic substances were removed on washing the diluted ethereal extract with alkali; it was subsequently washed with water, dried, and evaporated, and the residue adsorbed from benzene solution on alumina. Elution of the chromatogram with benzene gave a pale yellow, green fluorescent solution and the subsequent ethereal washings were added to the original benzene extract. The solid product obtained on evaporation of the benzene eluate on trituration with cold ether gave a pale yellow substance, which, after an elaborate purification, yielded an almost colorless *picene* derivative, m. p. 274-276° (Found: C, 93.8; H, 6.15. $C_{25}H_{20}$ requires C, 93.7; H, 6.3%).

The original benzene extract, together with the ethereal eluate from the chromatogram, was evaporated, and a benzene solution of the residue was absorbed on alumina. The solid (3.1 grams) from the first 2500 cc. of eluate was taken up in light petroleum (b. p. 40-60°)-benzene (1:1) and refractionated through alumina. The initial and the final runnings, which contained waxy and gummy substances, respectively, were neglected; two of the remaining fractions, after elaborate processes involving washing, crystallization, sublimation, and readsorption on alumina, ultimately yielded two substances. (a) A *chrysene* derivative, m. p. 172-173° [Found: C, 93.6; H, 6.5; $M(R_{\text{ast}})$, 279. $C_{21}H_{18}$ requires C, 93.3; H, 6.7%; M , 270]. (b) A *hydrocarbon*, m. p. 227° (Found: C, 92.6; H, 7.4. $C_{25}H_{24}$ requires C, 92.5; H, 7.4%), giving a 2,7-dinitroanthraquinone derivative, m. p. 242-243°.

Resolution of the sterol mixture.—The sterol mixture (950 mg.) was refluxed for 1 hour with acetic anhydride (10 cc.) and pyridine (10 cc.). The product, isolated by pouring into water, yielded two acetates on fractional crystallization: A (600 mg.), m. p. 123.5°, $[\alpha]_D^{20} - 41^\circ$ (c, 2.3), and B (50 mg.), m. p. 114-116°, $[\alpha]_D^{20} - 28^\circ$ (c, 1.5). A mixture of these two acetates in approximately equal amounts had m. p. 116-119°.

Sterol A (β -sitosterol).—Hydrolysis of acetate A with methyl-alcoholic potassium hydroxide (5%) yielded sterol A, which formed plates from methyl alcohol-acetone, m. p. 135-135.5°, $[\alpha]_D^{20} - 37^\circ$ (c, 1.6). $[\eta]$ (perbenzoic acid), 1.09. Benzoate: m. p. 147°, $[\alpha]_D^{20} - 15.2^\circ$ (c, 2.6). Reduction of acetate A in acetic acid with hydrogen and Adams catalyst at room temperature and pressure yielded the corresponding dihydroacetate, which formed plates from methyl alcohol-acetone, m. p. 128-128.5°, $[\alpha]_D^{20} + 11.5^\circ$ (c, 1.8). This, on alkaline hydrolysis, was converted into the dihydrosterol, m. p. 133-133.5°, $[\alpha]_D^{20} + 23^\circ$ (c, 2.5). Phenylurethane: m. p. 169-170°, $[\alpha]_D^{20} + 13.9^\circ$ (c, 1.6).

Sterol B.—The acetate B similarly gave sterol B in plates, m. p. 134°, $[\alpha]_D^{20} - 26^\circ$ (c, 2.1). $[\eta]$ (perbenzoic acid), 1.02. Benzoate: m. p. 145°, $[\alpha]_D^{20} - 14.9^\circ$ (c, 2.0). Reduction of acetate B under the above conditions gave a crystalline product, m. p. 122-123°, $[\alpha] - 8.2^\circ$ (c, 2.0), which, after alkaline hydrolysis, had m. p. 126.5-127°, $[\alpha]_D^{20} + 5.8^\circ$ (c, 1.2).

Ozonolysis of acetate B gave a volatile aldehyde, which was converted into the 2,4-dinitrophenylhydrazone. This, after purification through alumina and crystallization from alcohol, had m. p. 158-159°, undepressed by authentic acetaldehyde-2,4-dinitrophenylhydrazone (yield, 22%) (Found: N, 25.1. Calc. for $C_8H_8O_4N_4$: N, 25.0%). Ozonolysis of the dihydroacetate described above gave no acetaldehyde.

Sterol, B, on oxidation with aluminum *tert.*-butoxide and acetone in the usual manner, produced in small yield a ketone, m. p. 92-95° C. Light absorption in alcohol: Max. 2410 Å.; $\log \epsilon = 3.9$.

The red gum.—This material, when heated in a retort at 80-90/10⁻³ mm., gave a waxy distillate of eicosyl alcohol, which crystallized from methyl alcohol in leaflets, m. p. 62° C (Adam and Dyer¹⁰ give m. p. 65.0-65.5°). Acetate: needles, m. p. 41° (lit., 39.5-40.5°). *Phenylurethane*: plates from methyl alcohol, m. p. 75-76° (Found: C, 77.8; H, 11.3. C₂₇H₄₇O₂N requires C, 77.6; H, 11.3%). At 110-130° some crude sterol sublimed from the gum, and at 140-150° a pale yellow, viscous oil with ketonic properties distilled slowly. Volatile decomposition products were also evident, and the viscid residue in the retort had darkened in color and become insoluble in acetone. The distillate obtained at 140-150° was treated with 2,4-dinitrophenylhydrazine hydrochloride in alcohol, and the resulting red solid, dissolved in benzene, was towered on alumina. The benzene washings were evaporated, and the residue crystallized from benzene-methyl alcohol, giving scarlet prisms, m. p. 239-240° (Found: C, 70.9; H, 8.8. C₃₅H₅₂O₄N₄ requires C, 70.9; H, 8.8%). The mother liquor from the crystallization of the above substance contained a second 2,4-dinitrophenylhydrazone, which crystallized from light petroleum (b. p. 60-80°) in golden leaflets, m. p. 121-123°, but the analytical data for this material could not be interpreted.

The above work has been carried out as part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

SUMMARY

In previous studies of this material, the isolation and identification of a sterol, C₂₇H₄₆O,¹ and octadecyl alcohol⁹ have been described. It is now shown that the former is a mixture of isomeric sterols, which include β -sitosterol and probably a 24,28-dehydrostigmastanol, and that the aliphatic alcohol is eicosyl alcohol. No other pure component has yet been isolated in sufficient quantity for investigation, since the remainder of the neutral action undergoes extensive pyrolysis on distillation, even in a high vacuum. Evidence has, however, been obtained that a portion of the unsaponifiable substances becomes increasingly intractable as rubber ages, and it is possible that the present failure to obtain the ketone C₁₅H₂₄O and the so-called liquid sterols, C₂₇H₄₂O₃ and C₂₀H₃₀O, reported by Bruson, Sebrell, and Vogt⁹, may be due to this cause.

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THE ISOLATION OF AMINO ACIDS FROM RUBBER LATEX *

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After an examination of the chemical composition of the "resin" of rubber had been carried through,¹ there was initiated a chemical examination of the aqueous serum left on separating rubber from the latex of *Hevea brasiliensis*. This latter was carried as far as a study of the amino acids present, and had then to be interrupted. As it has not been possible since to resume it, and as several papers on the amino-acid composition of the proteins of *Hevea* latex have recently appeared, it is now thought desirable to put on record the results which were obtained.

While several investigations, mentioned below, have been made of the amino acids derived by hydrolysis from the proteins of rubber and latex serum, only one previously published investigation has been concerned with the amino acids present as such in latex. McGavack & Rumbold² isolated *d*-alanine from latex serum and secured some evidence of the presence of phenylalanine. In the present investigation, the following seven amino acids were isolated from the serum: tyrosine, *l*-leucine, *d*-iso-leucine, *d*-valine, *d*-arginine, *l*-aspartic acid and *i*-proline. Indications were also obtained of the presence of phenylalanine.

It may be noted that one of these, *d*-valine, was previously isolated from the acetone extract of rubber (sheet form).¹ Clearly, it had been taken up by the coagulum from the serum, and had escaped complete removal in the preparation of the rubber.

It is interesting to compare these findings as to the free amino acids present in *Hevea* latex with the results of the examination by various investigators of the amino acids obtained by the hydrolysis of protein from rubber and serum. Belgrave³ obtained evidence of the presence of glycine and proline in proteins obtained (1) from latex serum by precipitation with alcohol, and (2) from rubber by exhaustive extraction with benzene. Later work by Belgrave⁴ on the former protein indicated the presence, in addition, of arginine (in high proportion), cystine, histidine and lysine. Midgley, Henne and Renoll⁵ obtained the following from protein isolated from rubber: glycine, proline, arginine, histidine, lysine, leucine, aspartic acid and a representative of the group comprising alanine, phenylalanine, hydroxyproline and serine. They state that the following were definitely absent: cystine, glutamic acid and tyrosine. Subsequent authors, however, working it is true with protein isolated from rubber or latex in different ways, have identified these three amino acids in hydrolysates.

In protein obtained from latex serum by precipitation with ammonium sulphate, Altman⁶ identified and estimated proline, arginine, histidine, leucine, aspartic acid, alanine, dihydroxyphenylalanine, tyrosine, glutamic acid, hydroxyproline and valine. Tristram⁷ analyzed protein obtained by extraction of dried, fresh latex for the following nine amino acids, all of which were present, and which in total constituted about 50 per cent of the protein: arginine, histidine, lysine, aspartic acid, tyrosine, glutamic acid, cystine, methionine and tryptophan.

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TABLE I
AMINO ACIDS IN LATEX AND FROM LATEX PROTEINS

Proteins isolated by

1. Precipitation of serum with alcohol.
2. Precipitation of serum with ammonium sulfate.
3. Heat coagulation of serum.
4. Extraction of dried latex.
5. Separation from rubber.
6. Separation from rubber.

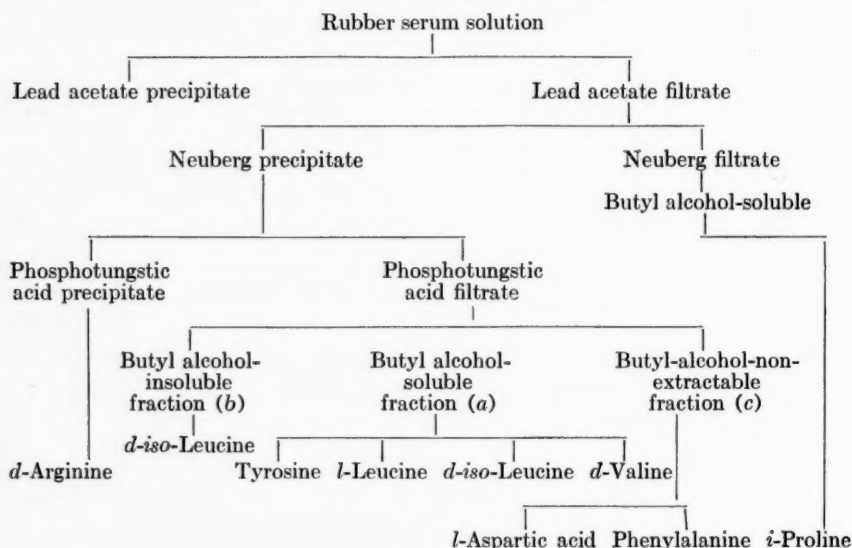
In latex serum		By hydrolysis of proteins					
McGavack and Rumbold ²	Present authors	1 Belgrave ¹	2 Altman ⁶	3 Present authors	4 Tristram ⁷	5 Belgrave ³	6 Middley <i>et al.</i> ³
Alanine	—	Glycine	Alanine	Glycine	—	Glycine	Glycine
—	—	—	Valine	—	—	—	—
—	—	—	Leucine	—	—	—	Leucine
Phenylalanine	—	—	—	—	—	—	—
—	—	—	Dihydroxyphenylalanine	—	—	—	—
—	—	—	Tyrosine	Tyrosine	Tyrosine	—	—
—	—	—	Aspartic acid	Aspartic acid	Aspartic acid	—	Aspartic acid
—	—	—	Glutamic acid	Glutamic acid	Glutamic acid	—	—
—	—	Arginine	Arginine	Arginine	Arginine	—	Arginine
—	—	Histidine	Histidine	Histidine	Histidine	—	Histidine
—	—	Lysine	—	Lysine	Lysine	—	Lysine
—	—	Proline	Proline	Proline	—	Proline	Proline
—	—	—	Hydroxyproline	—	Tryptophan	—	—
—	—	Cystine	—	Cystine	Cystine	—	—
—	—	—	—	Methionine	Methionine	—	—

In the present work a cursory examination of the heat-coagulable protein of latex serum led to the isolation from its hydrolysate of glycine, proline, aspartic acid, glutamic acid and tyrosine, and gave evidence of the presence, in addition, of histidine, arginine and lysine.

Table I summarizes the results of investigations made to date on the identification, isolation and estimation of the amino acids of rubber, latex and latex serum.

In isolating, in the present investigation, amino acids from latex serum, the method of fractionation employed was essentially that of Vickery⁸ and of Vickery and Leavenworth⁹, in which use is made of the mercuric acetate-sodium carbonate reagent of Neuberg and Kerb¹⁰ to precipitate the amino acids as their carbonates and the purines as mercury complexes. The chief modification introduced was in the separation of the monoamino acids and proline from the bases

TABLE II
OUTLINE OF FRACTIONATION PROCEDURE



and dicarboxylicamino acids. For this separation, use was made of the butyl alcohol extraction procedure of Dakin¹¹, which has proved so successful when applied by that worker to acid hydrolysates of proteins. The results of applying this procedure to the present case, however, were in keeping with the experience of Hunter¹², who found that a sharp separation could not be obtained with enzymic digests of proteins containing peptide material. It is indeed hardly surprising that the butyl alcohol extraction method did not follow the same course, and was not as complete and clear cut with the present material as with a protein hydrolysate, because of the presence, in addition to amino acids, of a host of other organic and inorganic compounds. There is, for example, little doubt that acid-hydrolysable peptides were present, as Vickery has shown to be the case with alfalfa juice. Nevertheless, in spite of these circumstances, the method was of value, and made it possible to isolate and identify tyrosine, *l*-leucine, *d*-iso-leucine, *d*-valine, *d*-arginine, and *i*-proline. The general scheme of fractionation is outlined in Table II.

Every attempt to arrive at the composition of a complex organic mixture of biological origin, such as a solution of chemical entities constituting a plant juice, requires in the first instance much preliminary pioneering work to determine what substances and groups of substances are actually present. In the initial stages of the present study, an attempt was made to keep an audit of the nitrogen separation, but many of the fractions obtained proved on further investigation to be so intractable that this had soon to be abandoned.

EXPERIMENTAL

A sample of serum solids, supplied by the Central Rubber Station, Buitenzorg, Java, and prepared by evaporating serum obtained by the coagulation of fresh latex with acetic acid, was used in some preliminary experiments. It was found that, although originally completely water-soluble, an appreciable amount had become insoluble during evaporation and storage. This insoluble material was isolated by filtration, washed with hot water, and dried. The resulting hard, dark brown material had no melting point, and was found to be protein in nature with 2.15 per cent ash. Repeated solution in sodium hydroxide and precipitation with acid gave a fairly white product. It will thus be seen that originally this protein was a normal soluble component of rubber latex, and that, whereas it was not precipitated by acetic acid (in the cold) during the coagulation of latex, subsequent heating had denatured it.

According to the view of Belgrave^{3, 4} and of Belgrave & Bishop¹³, the non-protein nitrogenous compounds in latex are destined for the synthesis of proteins, or are their decomposition products. If this be true, then an analysis of the protein for component amino acids should give helpful information as to nitrogenous substances which might be expected to occur in the free state in latex serum. With this object in view, a cursory examination of the protein was made.

The protein (100 grams) was hydrolyzed with six times its weight of 38 per cent sulfuric acid for 24 hours. The mineral acid was removed by adding baryta to pH 3, and the solution of amino acids was concentrated to 350 cc., when tyrosine began to crystallize out. The solution was then brought to pH 5.5 with potassium hydroxide and concentrated to 200 cc. After 18 hours at 0°, the separated material was filtered off. On repeated crystallization from hot water, this gave 2.5 grams of pure tyrosine.

The concentrated solution of amino acids was then subjected to a continuous butyl alcohol extraction¹¹. The fraction separating from the butyl alcohol (mono-amino-monocarboxylic acids, aliphatic and aromatic) weighed 31 grams. From this mixture, glycine was isolated as the ethyl ester hydrochloride: M.P. 144°.

The fraction soluble in butyl alcohol (proline and hydroxyproline) weighed 5.14 grams. Some difficulty was experienced in isolating proline as hydantoin, but evidences of its presence were found. The fraction not extracted by butyl alcohol was, after removal of the solvent, passed through the Foreman¹⁴ procedure for the separation of the dicarboxylic acids. In this way 11.4 grams of copper aspartate and 1.75 grams of glutamic acid hydrochloride (M.P. 196-197°) were obtained. The base fraction obtained from the Foreman filtrate by precipitation with phosphotungstic acid was examined by the Kossel procedure as given by Plimmer¹⁵ and although, for various reasons, the analysis was not completed, evidence of the presence of arginine, histidine and lysine was obtained.

From the cursory examination of the protein described above, it will be seen that it is quite similar to most plant proteins, and, on the hypothesis of Bel-

grave, gives hints as to the possible amino acids present in the serum of *Hevea brasiliensis*.

The actual work on serum solids was done on a quantity of serum solution (kindly furnished by the Naugatuck Chemical Company) obtained from latex preserved with ammonia and containing sodium alginate, which had been used to cause separation of the rubber by creaming. An attempt was made to evaporate this serum solution *in vacuo*, but the presence of sodium alginate caused violent frothing, and it was necessary to concentrate from 55 gallons to 10 liters at atmospheric pressure and 75° with the aid of constant stirring and an electric fan to carry off the vapor. The time taken was 74 hours, and during the concentration about 2 kilograms of rubber separated in small flocks, which were removed, together with coagulated protein, by skimming. Towards the end of the operation, magnesium oxide was added to remove ammonia. Finally, the cooled concentrate was diluted with alcohol to precipitate the residual rubber and protein, together with the major part of the alginic acid, which could then be filtered off. To the filtrate were added 1200 grams of normal lead acetate to remove proteoses and inorganic acids having insoluble lead salts and, also, to help

TABLE III

	Grams in 3800 cc.	Percentage of total nitrogen
Total nitrogen	124.6	100
Ammonia nitrogen	17.4	14
Amide nitrogen	4.1	3.3
Amino nitrogen	23.4	18.5
Other nitrogen	80.0	64.1
Solids	2180.0	—
Ash	286.0	—

clarify the solution under investigation. Not much precipitation occurred, however, until the solution was diluted with water. The precipitate was filtered, washed, and the filtrate and washings were saturated with hydrogen sulfide to remove lead. The clarified solution was then concentrated *in vacuo* at 30° in the presence of charcoal, filtered and made up to a volume of 10 liters. Of this, 3800 cc. were taken for further investigation, and the results of a preliminary analysis by standard methods are given in Table III.

PRECIPITATION WITH NEUBERG'S REAGENT

The solution was mechanically stirred and 40 per cent sodium carbonate added until the liquid was acid to phenolphthalein but alkaline to litmus. After standing 2 hours, 21 grams of inorganic solids were removed by filtration. To the filtrate were added in small alternate quantities 1900 grams of sodium carbonate (10 per cent solution) and 4750 grams of mercuric acetate (25 per cent solution) until red mercuric oxide began to separate. After a day at 4-5°, the voluminous precipitate was filtered off and washed with 80 per cent alcohol. The filtrate and washings were combined, and will be referred to later as the "Neuberg filtrate".

The Neuberg precipitate was suspended in as small a quantity of water as possible and treated with hydrogen sulfide. When the liberation of the nitrogenous material was complete, the solution was kept at 70° for a number of hours to granulate the mercuric sulfide. After filtering and washing with hot water, the filtrate and washings were concentrated *in vacuo* at 35°, and the volume made up to 2 liters. The analysis at this stage is given in Table IV.

On comparing Tables III and IV, it will be seen that the Neuberg precipitate has carried down 82 per cent of the total nitrogen of the original solution, and that the amide nitrogen has disappeared, probably by hydrolysis in the alkaline medium, thus augmenting the yield of ammonia nitrogen.

Sulfuric acid was next added to the above-mentioned solution obtained from the Neuberg precipitate until the concentration of the acid was 5 per cent; this was followed by 25 per cent aqueous phosphotungstic acid containing 5 per cent sulfuric acid, added in small quantities at a time with stirring, until a drop of the supernatant liquid gave a white precipitate with a drop of baryta. The reaction mixture was kept at 5° for 50 hours, filtered and the precipitate washed well with 5 per cent sulfuric acid. The procedure up to this point has separated the original solution of serum solids into three fractions (see Table I):

(a) "Neuberg filtrate": a fraction containing nitrogenous substances not precipitated by mercuric acetate-sodium carbonate.

(b) "Phosphotungstic acid precipitate": a fraction containing nitrogenous substances precipitated by mercuric acetate-sodium carbonate and by phosphotungstic acid, *viz.*, purines, diamino acids.

TABLE IV

	Grams in 2.1 cc.	Percentage of total nitrogen
Total nitrogen	101.9	100
Ammonia nitrogen	19.0	18.65
Amide nitrogen	None	None
Amino nitrogen	23.9	23.5
Other nitrogen	59.0	57.9
Solids	1094.2	—
Ash	211.8	—

(c) "Phosphotungstic acid filtrate": a fraction containing nitrogenous substances precipitated by mercuric acetate-sodium carbonate but not by phosphotungstic acid, *viz.*, monoamino acids.

NEUBERG FILTRATE

The Neuberg precipitate having been removed, the filtrate was diluted with an equal volume of 95 per cent alcohol (18 liters) and kept for 24 hours, after which some mercuric acetate was removed as a coordination compound with mercuric oxide¹⁶. The filtrate was now acidified with acetic acid, and hydrogen sulfide passed in to remove traces of mercury. After filtration, the combined filtrate and washings were concentrated *in vacuo* at 35° to 8 liters. Since 1900 grams of sodium carbonate had been introduced into this solution during the Neuberg precipitation and, since the sodium was now present in the form of both acetate and carbonate, the following method was used to remove the sodium ion as chloride and the acetate ion as acetic acid.

The solution was first acidified to pH 3 with hydrochloric acid. This caused the separation of a large quantity of sodium chloride and liberated all the acetic acid. The salt was removed by filtration and the filtrate concentrated until sufficient sodium chloride had separated to make the vacuum distillation difficult. The salt was again removed and distillation continued. In this way practically all the acetic acid was removed, and the volume of the solution reduced to 2.5 liters. At this point 2.5 liters of 95 per cent alcohol were added to the concentrate, whereby 500 grams of sodium chloride and potassium chloride were

removed. The clear filtrate was reduced *in vacuo* to 1 liter and an equal volume of alcohol added. This threw down much quebrachitol and some inorganic material. These were filtered off and washed with alcohol. The filtrate and washings were concentrated to remove all alcohol, and then submitted to the continuous butyl alcohol extraction of Dakin¹¹ for 200 hours to remove any proline that might have escaped precipitation by the Neuberg reagent. It was found that the butyl alcohol extracted a fair amount of material, including most of the pigment, from the aqueous solution, and that on removing the solvent the resulting thick paste was very soluble in water. Five grams of this paste were treated for proline by the method of Dakin¹¹. To the solution in 50 cc. of water 8 grams of potassium cyanate were added and the whole was evaporated to dryness on a water bath. The mass was taken up with water and acidified with sulfuric acid until acid to Congo red (*pH* 3). The solution was then extracted with ether for 7 hours in a continuous extractor¹¹ to remove monoamino acids, if present. When the extraction was complete, one-fifth volume of 50 per cent sulfuric acid was added and the solution heated on the water bath for 2 hours to convert the proline into the hydantoin. The solution was again extracted with ether for 50 hours when there were obtained 26 mg. of substance which melted at 141-144°. The melting-point of *i*-proline hydantoin is given by Dakin¹¹ as 143°. (Found by Folin's colorimetric method¹⁷: N, 21.1 per cent; $C_6H_8O_2N_2$ requires N, 20.0 per cent.) The small yield did not permit of further confirmatory evidence being obtained. Small-scale experiments using mercuric chloride gave no evidence for the presence of betaines in this fraction.

PHOSPHOTUNGSTIC ACID PRECIPITATE

The wet precipitate was suspended in 3 liters of water and decomposed by adding baryta until alkaline to litmus. The magma was kept warm for 3 hours, filtered, the barium phosphotungstate well washed with hot water and the filtrate and washing reduced *in vacuo* to 3 liters. The last trace of barium was now removed in the usual way, and the final volume adjusted to 2 liters. This is the "purine and diamino-acid fraction", which analyzed as follows:

	Grams
Total solids	203.6
Ash	98.4
Total nitrogen	18.6

The fraction was treated with silver nitrate (120 grams), which threw down a very dense canary yellow precipitate of purine-silver nitrate complexes. This was filtered, washed with hot water and decomposed with hydrogen sulfide. The filtrate on evaporation gave 91 grams of a mixture of yellow crystals and a dark-brown syrup having an ash content of 65.1 per cent, the residue being almost pure tungstic oxide. The mixture contained 2.8 grams of nitrogen, but attempts to separate the purine bases from it were unsuccessful.

The histidine fraction.—The above-mentioned filtrate, which might contain the three bases, was submitted to the usual Kossel procedure for their isolation. Baryta was added until a drop of supernatant liquid no longer gave a white precipitate with a reagent made by adding ammonia to a 10 per cent silver nitrate solution until the silver just dissolves. The precipitate was kept in the cold for several hours before filtering and washing with cold water. It was then decomposed with hydrogen sulfide and the clarified filtrate taken to dryness *in vacuo*;

1.5 grams of a light lemon-yellow solid were obtained, which gave none of the usual reactions for histidine. It is inferred, therefore, that the latex serum does not contain this base.

The arginine fraction.—The base solution was next saturated with baryta at 40°. After several hours the arginine-silver complex was separated by filtration, decomposed in the usual way and concentrated under reduced pressure. The solid material thus obtained weighed 4 grams, and the ninhydrin test showed that α -amino nitrogen was present. Arginine was obtained from it as flavianate by the method of Vickery¹⁸ and, for further characterization, was converted into the carbonate by the method of Pratt¹⁹. The yield of white crystalline material was 1.42 grams: 0.2410 gram when heated at 105° for 4 hours lost 0.104 gram, showing the presence of 0.5 molecule of water of crystallization (no previous reference in the literature). For the air-dried material: C=37.6; H=6.66 per cent. $C_7H_{14}O_4N_4 \cdot 0.5 H_2O$ requires C, 36.95; H, 6.61 per cent. For the anhydrous material: N=25.15 per cent. $C_7H_{14}O_4N_4$ requires N, 25.7 per cent. The silver salt of arginine was made from 0.2 gram by adding sufficient nitric acid to form the mononitrate, and then adding the equivalent of silver nitrate. On diluting with alcohol, then with ether, and keeping the mixture in the dark, white needles separated slowly (M.P. 181-183° with decomposition; Riesser²⁰ gives 183°). Found: Ag, 26.64 per cent. $C_6H_{11}N_4O_2 \cdot HNO_3 \cdot AgNO_3$ requires Ag, 26.15 per cent. The picrate melted at 203-205° (Mulliken²¹ 205-206°) and the anhydrous copper salt at 238-240° (Riesser²⁰ 232-234°). A solution made by dissolving 1 per cent of the carbonate in 5 per cent hydrochloric acid showed in a 1 dm. tube $[\alpha]_D^{20} + 9.1^\circ$.

From the above evidence, it is certain that the compound isolated was *d*-arginine, and that it therefore occurs as such in the original solution of serum solids.

The lysine fraction.—Silver and barium were completely removed from the arginine filtrate, and the clarified solution was concentrated to 510 cc. The mercuric chloride-baryta treatment of Winterstein²² gave 5 grams of a dark brown hygroscopic mass, from which it was not found possible to isolate lysine as its picrate. Other attempts to obtain some evidence for the presence of this base also failed.

PHOSPHOTUNGSTIC ACID FILTRATE

The amino acid fraction which was precipitated by Neuberg's reagent, but not by phosphotungstic acid, was submitted to continuous extraction with butyl alcohol to give:

- (a) A fraction soluble in butyl alcohol.
- (b) A monoamino acid fraction insoluble in, but extracted by, butyl alcohol.
- (c) A monoaminodicarboxylic acid fraction not extracted by butyl alcohol.

It must be stated that this extraction was by no means as clear cut as in the case of hydrolyzed proteins for which it was primarily designed, but even so a sufficient separation of material was obtained to lead to the isolation of a number of amino acids.

The extraction was continued for 200 hours, the butyl alcohol being changed every 24 hours. At the end of each day the butyl alcohol was filtered to remove Fraction (a) (see above) and the residue washed with fresh alcohol. The filtrates were collected, the alcohol was removed *in vacuo*, and the residue was taken up in water (Fraction (b)). The aqueous solution of unextracted material was evaporated *in vacuo* to remove butyl alcohol and some acetic acid, and there was thus obtained a thick golden yellow paste (Fraction (c)).

Fraction (a).—The solution (500 cc.) on standing deposited 4.4 grams of nearly colorless crystals which gave a strong Millon reaction, indicating the presence of tyrosine. The material was suspended in 150 cc. of 95 per cent alcohol and boiled, water being added slowly until no more of the suspension went into solution. The residue was filtered off and washed with alcohol. The dried material (0.69 gram) was dissolved in hot water, treated and norit (0.1 gram), filtered, and concentrated on the water bath to incipient crystallization. On cooling, characteristic crystals of tyrosine separated, and were filtered off (0.41 gram). The mother liquor on further concentration yielded an additional 0.11 gram. The Millon test was positive. (Found: C, 59.9; H, 6.0; N, 7.69 per cent. $C_9H_{11}O_3N$ requires C, 59.7; H, 6.1; N, 7.73 per cent.) On standing, the solution from which the crude tyrosine had separated deposited thin lustrous crystals. These were filtered off and washed with cold alcohol (1.62 gram). Millon's test was negative, showing the absence of tyrosine. Their greasy feel, the fact that they were moistened by water only with difficulty, and especially their analysis, suggested that they were leucine (found: N, 10.68; amino-N, 10.94 per cent; mol. wt. (freezing point of water) 126.7; $C_6H_{13}O_2N$ requires N, 10.7; amino N, 10.7 per cent; mol. wt. 131), but the specific rotation in water, $[\alpha]_D^{20} - 13.6^\circ$, was too low and in 20 per cent hydrochloric acid was too high $[\alpha]_D^{20} + 27.1^\circ$, the recorded values in the literature being -10.42° and $+15.53^\circ$, respectively. Further investigation showed that the product was a mixture, and *l*-leucine was identified as its phenylhydantoin, M.P. 119-120°, and *d*-iso-leucine as its benzoyl derivative, M.P. 116°.

The mother liquor from the above separation was concentrated to a syrup and kept at 0° for 24 hours. A mass of crystalline material was deposited, which was filtered off and washed with ethyl acetate. The product (6.73 grams) was recrystallized from hot water to give ill-defined colorless platelets (2 grams), which were subsequently shown to be a mixture of *l*-leucine and *d*-iso-leucine. The final mother liquor was taken to dryness (473 grams), dissolved in the minimum quantity of water, and treated with much alcohol. On standing, another crop of crystalline material (2.6 grams) was obtained. This was filtered off, dissolved in water and precipitated by adding a large volume of alcohol. The product was *d*-valine. (Found: C, 50.4; H, 9.45; N, 11.88 per cent. $C_5H_{11}O_2N$ requires C, 51.3; H, 9.40; N, 11.96 per cent.) The specific rotation in water was $[\alpha]_D^{20} + 6.3^\circ$ and in 20 per cent hydrochloric acid $[\alpha]_D^{20} + 28.6^\circ$, while the phenyl-carbamido acid melted at 154-153° and the phenylhydantoin at 129-130.5°, values in keeping with those in the literature.

Fraction (b).—This weighed 7.8 grams and contained 30 per cent of ash. Two grams of the material were dissolved in 10 cc. of *N* sodium hydroxide, and to the cooled solution an equivalent of phenylisocyanate was added. The mixture was shaken, with cooling, until the odor of isocyanate had disappeared. After filtration, the phenyl-carbamido acids in the filtrate were precipitated by adding 10 cc. of *N* hydrochloric acid. On recrystallization, 1 gram of the phenylcarbamido derivative of *iso*-leucine, M.P. 119-120°, was obtained. The hydantoin obtained by dehydration with hydrochloric acid melted at 80°.

Fraction (c).—After standing for about two months, this fraction showed no signs of crystallization; it was therefore saturated with gaseous hydrogen chloride, which precipitated much sodium and potassium chlorides. These were removed by filtration, and the filtrate set aside at 4-5° for 5 weeks, but no glutamic acid separated. A similar result was obtained in attempting to isolate glycine ethyl ester. The material was therefore collected, water removed, the residue covered

with 4 volumes of 95 per cent alcohol and saturated with dry hydrogen chloride to precipitate most of the inorganic material (150 grams) and to bring the remainder into solution (as ethyl ester). After filtration, the alcohol and water were then removed *in vacuo*, 4 volumes of absolute alcohol were added, and the mixture again saturated with gaseous hydrogen chloride.

The esterified solution was evaporated almost to dryness under reduced pressure, and the residue dissolved in the smallest quantity of water. The esters were liberated with sodium hydroxide and extracted with ether, after saturation of the liberated ester solution with potassium carbonate. When the greater part of the dry ether was evaporated, 6 volumes of distilled water were added, and the solution was refluxed for 6 hours to hydrolyze the esters to the free amino acids and ethyl alcohol. Ordinary distillation removed most of the alcohol, and evaporation under reduced pressure left a solid residue weighing 38 grams and also gave a turbid distillate from which were obtained 2 cc. of a pungent smelling oil. This oil was set aside to be investigated at a future date. The solid residue was dissolved in as little hot water as possible, and decolorized with animal charcoal. To the clear filtrate 500 cc. of acetone was added, which caused the separation in two crops of 16 grams. of material, M.P. 259-263°. Appropriate tests showed that this contained no glutamic acid, but that the ninhydrin reaction was positive. Negative Millon and positive xanthoproteic tests indicated the presence of phenylalanine. It was found, after a great deal of experimentation, that this material was not completely soluble in cold glacial acetic acid; 4 grams were accordingly suspended in cold glacial acetic acid and filtered rapidly, the residue being washed repeatedly with small quantities of the acid. In this way 1.04 grams of a pure white crystalline substance were obtained. Analysis of the substance, and of its insoluble copper salt, showed that it was *l*-aspartic acid. (Found: C, 36.4; H, 5.27; N, 10.58 per cent; $C_4H_7O_4N$ requires C, 36.1; H, 5.26; N, 10.52 per cent.) The specific rotation in 1 per cent aqueous solution was $[\alpha]_D^{20} - 4.1^\circ$. The copper salt contained 23.0 per cent Cu; $C_4H_5O_4NCu \cdot 4 \cdot 5H_2O$ requires Cu 23.05 per cent.

SUMMARY

The following amino acids are shown to occur in the serum of the latex of *Hevea brasiliensis*, all except the last having been actually isolated from it: tyrosine, *l*-leucine, *d*-iso-leucine, *d*-valine, *d*-arginine, *l*-aspartic acid, *i*-proline, and phenylalanine. A cursory examination of the amino-acid composition of the heat-coagulable protein of latex has been made. A tabular summary is given of the results obtained by various workers to date on the amino-acid composition of latex and latex proteins.

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APPLICATION OF THE LANGMUIR TROUGH TO THE STUDY OF RUBBER LATEX *

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When a drop of ammoniated latex is allowed to touch a cleaned water surface, it spreads rapidly and evenly at the air-water interface, none entering the bulk of the water. Microscopic examination of such a film shows that, given sufficient spreading area, the latex globules are clearly separate one from another, and form a layer one particle thick. On reducing the area occupied by the globules by compressing the film between waxed glass straight edges lying in the surface of the water, the particles are forced together until visible spaces or voids disappear. The film still appears to be one particle thick, and remains in the surface of the water. Further compression results in irregularities of the surface, which can be seen to consist of folds in the film and, on expansion, a proportion of the latex globules is found to have been forced from the surface into the bulk of the water. If a dilute solution of certain substances is used in place of water, the latex particles all remain on the surface, even under conditions of high compression. Dilute acids and solutions of divalent metal salts are found to be effective in keeping the particles in the surface but, on compression to the point where close packing of the particles occurs, the film sometimes forms a continuous coagulum and on release of the pressure, it does not expand. Solutions of a creaming agent, such as 0.1 per cent sodium alginate (Manucol V), are adequate, not only to prevent particles being forced out of the surface, but also to give films which expand readily on release of the pressure. The fact that the latex is instantly swept to one side by a trace of surface active material, such as oleic acid, confirms that the particles have not penetrated into the interior of the water.

ESTIMATE OF PARTICLE SIZE

It is apparent that, if the quantity of rubber added as latex to the surface is known and the area occupied by the surface film when the particles appear to be touching is measured, a value for the average thickness of the rubber film can be obtained, or more strictly:

$$\frac{\sum n \frac{4}{3} \pi r^3}{\sum n \pi r^2}$$

that is, the total volume of the particles divided by the total area of cross-sections, n being the number of particles of radius r . Attempts were made to determine the area occupied by the globules for a known weight of latex when closely packed, but the results obtained could not be repeated with any degree of accuracy, owing to the difficulty of observing the compressed surface layer. This was due to the rather poor resolution obtained with the microscopic equipment; the substage condenser had to be placed below the trough containing the solution, the light passing through a glass window in the bottom and through the solution

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before reaching the layer under observation. The measurements made on a 0.1 per cent solution of sodium alginate are given in Table I.

It will be seen that the measurements of film thickness did not give reproducible results, and the figures obtained are to be regarded as approximations rather than accurate values. For preserved field latex, the average thickness of the layer was found to be 0.9 microns, which is much higher than a value of 0.44 microns, calculated from figures obtained by Lucas¹ for preserved field latex, using ultraviolet photomicrographs. Examination of a film at the area corresponding to an average thickness of 0.44 micron showed, however, that the particles were well separated by voids. If the small particles are invisible under the microscope or were overlapped by larger ones, it can be calculated that all particles less than 0.6 micron would have to make no contribution to the area to account for the discrepancy between the two sets of data. There is, therefore, no doubt that the average particle size of this latex is much larger than that calculated from Lucas's data.

TABLE I

TABLE 1				Average thickness of layer $\frac{\sum n \frac{4}{3} \pi r^3}{\sum n \pi r^2}$ (microns)
	Latex	Close-packing area (sq. cm.)		
0.03 cc. of	ammonia-preserved field latex, diluted to 20 per cent dry rubber content	1.	70-84	0.9
		2.	63-70	
0.03 cc. of	centrifuge skim, creamed, and diluted to 20 per cent dry rubber content	1.	98	0.7
		2.	64	

SURFACE-PRESSURE MEASUREMENTS

Measurements of the surface-pressure developed by rubber latex at an air-water interface were carried out, using a waxed Pyrex glass trough containing a 0.1 per cent solution of sodium alginate. For each experiment, 0.02 cc. of 20 per cent latex was delivered from a micrometer syringe into the cleaned surface, and was allowed to spread over an area for approximately 170 square centimeters. A simple form of pressure recording apparatus² was used, consisting of a waxed barrier rigidly connected to a simple torsion wire with a torsion head. It was found necessary to allow a period of at least ten minutes after adding the latex before a measurement of surface pressure was taken, in order that equilibrium should be attained. Gorter and Grendel³ have observed that protein films spread rather slowly, and this explains why latex films do not rapidly reach equilibrium. After the pressure had been recorded, the area of the surface was reduced to a given value and the pressure was again observed as soon as equilibrium was reached; a further decrease in area was then made, and so on. In this manner data were obtained for four Ceylon latices; (1) ammonia preserved latex, 37 per cent dry rubber content, (2) the same latex centrifuged to 60 per cent dry rubber content, (3) centrifuge skim from 2, recentrifuged to 50 per cent dry rubber content, and (4) centrifuge skim from 2, creamed to 35.5 per cent dry rubber content.

The results were found to be reproducible, and are shown in graphical form in the figure, in which surface pressure F (dynes per sq. cm.) is plotted as

ordinate against surface-area A (sq. cm.) as abscissa. The curves show a definite bend after the area has been reduced to about one-half the initial value. In the case of samples (1) and (4), the graph consists of two almost-straight lines, before and after the bend, the graphs of (2) and (3) being more hyperbolic in character. The areas at which the bends occur correspond approximately with the position of closest packing of the particles, determined microscopically. Thus the area at which close packing was observed for sample (1) was 46 sq. cm., the bend in the curve occurring at 48 sq. cm. This corresponds to a value for the average thickness of the rubber film of 0.9 micron. The order of the relative sizes of the particles in the four latices examined is known from the treatment which they received during preparation. Table II shows that the average thicknesses

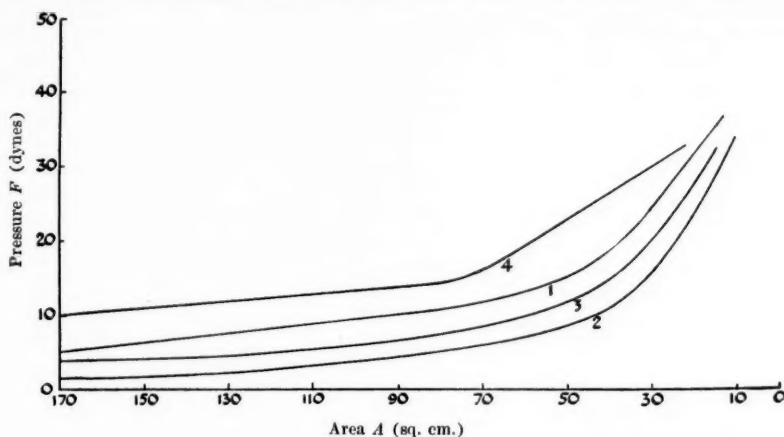


TABLE II

Latex	Area occupied by 0.02 cc. latex at bend (sq. cm.)	Average thickness of layer (microns)	Estimated surface- area of particles per g. of rubber ($\frac{2n}{3}\pi r^2$) (sq. cm.)
1.....	48	0.9	48,000
2.....	39	1.1	39,000
3.....	42	1.0	42,500
4.....	80	0.5	80,000

of the films, calculated from the area at the bends, are in the correct order, and it is thought that these values probably give a more accurate estimate of the particle size than those obtained by microscopic observation of close-packing.

It is of interest to note that the change in slope at the bend can be correlated with the quantity of serum substances present; thus sample (2), which is a centrifuged latex, contains the least serum substances and shows the greatest change, whereas sample (4), which is a centrifuge skim concentrated by creaming, contains a high proportion of serum substances and shows the flattest curve.

Table III shows the values of surface pressure for the four latices at different areas, and the quantities of serum substances present as calculated from the difference between total solids and dry rubber content. The ratios of these values are given and show that, at low compression, the figures for the pressure F follow almost exactly the same order as those for the quantity of serum substances, indicating that in this region of the curve the pressure is due to

the serum substances. As the compression is increased, the ratio of the values of F departs more and more from that of the serum substances, and it may be concluded that the latter part of the curve is influenced by another factor, most probably the packing and compression of the rubber globules. It was thought possible that an unstable surface film of rubber particles might be formed during compression, and experiments were carried out in which the surface layer was rapidly compressed by moving a barrier across the trough until a predetermined pressure was reached, with a view to obtaining readings before collapse of the film. The results were irregular, however, and the values were found to be a function of the rate of compression. As this was carried out by hand, reliable data were not obtainable; so far no experiments incorporating a mechanical means of moving the barrier have been attempted.

At this stage of the investigation, experiments were carried out to correlate the measurements made on the trough with empirical stability tests. Table IV shows results expressed as ratios, of (A) the proportion of serum substances present per unit of rubber; (B) surface pressures at the same surface concentration; (C) N_r and N_w values⁴ and (D) coagulation tests (*a*) by gelling with sodium silicofluoride, (*b*) by stirring with zinc oxide. It will be seen that there is a close parallelism between the various sets of data, save in the case of N_r values, which show rather different ratios. The agreement between trough measurements and coagulation tests was found to be better with sodium fluosilicate than with zinc oxide. The results indicate that both the stability tests and the surface pressure measurements are to a large extent dependent on the quantity of serum substances present and, further, that the surface pressure values are also an indication of the resistance to coagulation.

THICKNESS OF PROTEIN LAYER AT AIR-WATER INTERFACE

If it is assumed that the surface pressure set up by latex at an air-water interface is largely due to protein, the pressure due to a given surface concentration of latex protein may be calculated, but it is necessary to make certain assumptions regarding the space occupied by rubber particles and the distribution of protein between rubber-water and water-air interfaces. Belgrave⁵ gives the proteinic nitrogen in latex as about 50 per cent of the total, whereas Tristram⁶ found that 30 per cent of the nitrogen extracted from the dried film at pH 9.2 was proteinic. It is a debatable point whether in the trough experiments the protein associated with the globules would be removed and spread over the water surface or whether it would remain surrounding the particles; possibly the proportion around the particles varies with the surface pressure. Assuming, however, that the protein in the aqueous phase spreads at the water surface and that the protein surrounding the globules is not appreciably removed, the concentration of protein at the water surface for the four latices at a pressure of 5.5 dynes per cm. is shown in Table V, the amount of protein being estimated from N_w values determined by Baker⁷, using a factor of 6.25 and assuming that 30 per cent of N_w is proteinic. The figures given were obtained in the first case, assuming that the serum protein is spread over the whole of the water surface; in the second case, assuming that the available water surface is the area of the trough less the cross-sectional area of the rubber globules, as obtained from the close-packing area. The values of protein per unit area of water surface are higher than those obtained by Hughes and Rideal⁸, and by Tristram⁶ for latex protein, which are included in the table. In considering the values obtained, it must be borne in mind that surface-active substances other than protein, such as lipoids, are probably present.

TABLE III

Latex	Relative proportions of serum substances	Initial pressure F at 170 sq. cm. (dynes per cm.)	F at 120 sq. cm.		F at 90 sq. cm.		F at 68 sq. cm.		F at 34 sq. cm.	
			Dynes per cm.	Ratio	Dynes per cm.	Ratio	Dynes per cm.	Ratio	Dynes per cm.	Ratio
1.....	2.3	5.3	8.0	2.3	10.2	2.3	11.6	1.7	21	1.65
2.....	1.0	1.5	3.5	1.0	4.4	1.0	6.7	1.0	12.5	1.0
3.....	1.7	3.7	6.0	1.8	6.5	1.5	8.8	1.3	17.5	1.35
4.....	3.3	10.5	12.1	3.5	13.9	3.2	17.4	2.6	29	2.2

TABLE IV

Latex	Relative proportions of serum substances	Relative pressures at same surface concentration of latex in Langmuir trough (0.02 cc. per 120 sq. cm.)		Ratio of N_w for same total solids	Ratio of times to gell with sodium fluosilicate	Ratio of revolution to coagulate by stirring with zinc oxide
		2.3	3.5			
1.....	2.3	1.2	2.2	2.2	2.5	2.8
2.....	1.0	1.0	1.0	1.0	1.0	1.0
3.....	1.7	1.7	1.5	1.5	1.6	1.0
4.....	3.3	2.5	2.8	2.8	3.1	3.6

THICKNESS OF PROTEIN LAYER AT RUBBER-WATER INTERFACE

It is possible also to estimate from the experimental results the amount of protein associated with unit surface-area of the latex globules. The nitrogen associated with the rubber globule (N_r) may be assumed to be largely proteinic, as almost all of it can be removed by proteolytic enzymes, about 0.02 per cent of the rubber phase being firmly held even after treatment with hot caustic soda⁴, and is probably not proteinic. A small amount of the nitrogen in latex is also present as lipin (Rhodes and Bishop⁹) which may be absorbed at the surface of the particles. Calculating the protein approximately as $(N_r - 0.02) \times 6.25$, the values for the weight of protein per unit area of the rubber-water interface are given in Table VI.

TABLE V

Latex	Area at 5.5 (sq. cm.)	Protein at 5.5 dynes per cm. (g. per sq. cm.)	
		(a) based on area of trough	(b) based on area of trough less area occupied by particles
1.....	165	2.4×10^{-7}	3.4×10^{-7}
2.....	85	2.1×10^{-7}	3.9×10^{-7}
3.....	127.5	2.1×10^{-7}	3.1×10^{-7}
4.....	*300	1.7×10^{-7}	2.1×10^{-7}
Hughes and Rideal		at 5.5 dynes per cm.:	1.1×10^{-7}
Tristram		unpurified protein	
		at 0 dynes per cm.:	0.4×10^{-7}
		at 14 dynes per cm.:	0.8×10^{-7}
		purified protein	
		at 0 dynes per cm.:	1.0×10^{-7}
		at 10 dynes per cm.:	1.8×10^{-7}

* Extrapolated value.

TABLE VI

Latex	Surface area per g. rubber (sq. cm.)	Protein (g. per sq. cm. of surface of globules)	Thickness of protein layer (millimicrons)
1.....	48,000	1.8×10^{-7}	1.4
2.....	39,000	1.8×10^{-7}	1.4
3.....	42,500	2.8×10^{-7}	2.1
4.....	80,000	2.2×10^{-7}	1.7

The results show that for the parent field latex (1), the same latex centrifuged to 60 per cent dry rubber content (2), and for the centrifuged skim-creamed to 35 per cent dry rubber content (4), the amounts of protein per unit surface area are the same, within the limits of experimental error, thus indicating that particle size has little or no effect on the amount of protein associated with unit surface-area. The value obtained for latex (3) which was centrifuge skim recentrifuged to 50 per cent dry rubber content, was rather higher than the other values; no explanation of this result has yet been found. As the concentration of protein at the surface of the latex particles was found to be over 1.5×10^{-7} gram per sq. cm., it is probable that the protein in latex is in the compressed "gel" state, with the side chains tilted out of the plane of the rubber-water interface, the hydrophobic hydrocarbon side chains being tilted towards the rubber phase, the hydrophilic side chains containing carboxy or amino groups being tilted into the water phase.

The thickness of the protein envelope corresponding to the weight per unit surface, assuming a specific gravity for protein of 1.33, is about 1.5 millimicrons,

as shown in Table VI. In comparison with the diameter of an average sized latex particle, say, 0.5 micron, it will be seen that the protein layer has a thickness of about 0.3 per cent of the diameter and is, therefore, a relatively thin film.

LIPID-PROTEIN MONOLAYER

Rideal and Schulman¹⁰ and their coworkers have shown that protein monolayers in the presence of lipid substances form complexes when one material is injected beneath a monolayer of the other. Two distinct types are formed¹¹. "In one case the injected molecules penetrated the surface film to form a mixed equimolecular monolayer; in the other the injected molecules were absorbed on to the film to form a double layer." The first type of complex film is found when protein monolayers are spread in the presence of fatty substances¹², and as lipid materials are present in latex, such as lipin⁹, glyceride⁶ and fatty acids, the protein surrounding the globules may be associated with these substances to form a complex layer. It has been found that a mixture of cholesterol and gliadin yields a film of the first type mentioned above¹². On compression to about 4.7×10^{-7} gram per sq. cm., however, the protein is forced out of the surface layer and the second type of complex, a duplex film, is formed with cholesterol uppermost and gliadin in contact with the water. According to the values of surface area obtained in Table II, the concentration of proteinic and fatty substances associated with the surface of the latex globules may easily reach a value comparable to 4.7×10^{-7} gram per sq. cm., and it may be that the globules are surrounded with a duplex lipo-protein layer, with the fatty substances next to the rubber and the protein on the outside, next to the serum. Experimental evidence directly supporting this arrangement is found in the work of Kemp and Twiss¹³, who showed that the curve of mobility against pH for latex particles was almost identical with that for the latex protein alone; from their results these workers concluded that at a pH of 8 and above 12 per cent dry rubber content the latex globules were completely surrounded by protein, the fatty substances thus being covered as well. It was also shown that, in the case of dilute latices below a pH of about 7, the lower the pH of a given latex the greater was the proportion of the particle surface covered with protein. These results agree closely with the observation of Schulman and Hughes¹⁴ that no displacement of protein by fatty acids occurs in solutions more acid than pH 3 to 4; at pH 5.5 the rate was relatively slow, and became greater as the pH increased.

Experiments in this laboratory have shown that the addition of oleic acid to ammoniated latex gives rise to an increased resistance to coagulation by electrolytes, which probably indicates an increase in ζ -potential; further, it has been shown that the protein is almost entirely removed from the rubber globule⁴. These observations are in agreement with the results obtained by Schulman and Hughes¹⁴, who have found that, as well as penetrating a protein monolayer, fatty acids will disperse the fatty acid-protein complex thus formed, leaving a monolayer of fatty acid. This change is accompanied by an increase in the boundary potential, which corresponds with the observed indications of an increase in ζ -potential.

EFFECT OF NATURE OF SURFACE MONOLAYERS ON PROPERTIES OF LATEX

Summarizing the above, it may be suggested that by analogy with the behavior of lipo-protein monolayers at an air-water interface, the latex globule in ammoni-

ated latex is surrounded by a complex lipo-protein layer, which may take the form of a duplex film, the lipid portion being in contact with the rubber phase and the protein with the serum. Bearing this hypothetical picture of the latex globule in mind, it is of interest to visualize the changes which are likely to occur in the latex on storing. It is probable that the surface of the latex particle will tend to become more lipid in character as protein will gradually be hydrolyzed by the enzymes present, thus forming water soluble breakdown products which will pass into the serum¹⁵, leaving the surface layer with a higher proportion of fatty substances. Should the lipoids themselves be hydrolyzed by ammonia or by enzymes, the products of the reaction would probably contain fatty acids, which may be reabsorbed at the rubber-water interface. Baker's experiments have shown that to replace the protein entirely, at least five times as much soap is required, and that the quantity of fatty acid present in ammonia-preserved latex is not much more than 1 per cent. There is not sufficient fatty acid present in latex, therefore, to replace all the protein on the globule and, as the substances forming the surface layer are hydrolyzed, the amount of absorbed material per unit area of the rubber-water interface will decrease, allowing the interfacial film to expand, with consequent lowering of the surface pressure and probably of the ζ -potential. This is in agreement with the decrease in resistance to coagulation observed in latex on storage. If, however, sufficient fatty acid is added to latex, a fatty acid-protein complex will first be formed, followed by dispersion of the protein layer, the fatty acid also penetrating the lipid layer¹⁶. In consequence, the surface of the particle would become more hydrophobic and the ζ -potential would be increased, giving an increased resistance to coagulation. As the isoelectric point of the lipid portion (pH=2.1) is lower than that of the protein (pH=4.4)¹³, it is to be expected that the pH at which coagulation of the latex occurs would be lowered. Experiments have shown this to be the case.

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RHEOLOGIC AND ELASTOMETRIC MEASUREMENTS OF RUBBER PRODUCTS *

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The great majority of the methods in current use in the rubber industry for judging the plastic and elastic properties of rubber products are open to the same fundamental objection, namely, that the experimental results are expressed in arbitrary units rather than in the c.g.s. system. This can be explained by the fact that a specialist concerned with measurements of this kind has not, up to the present time, had at his disposal any instruments for measuring the desired properties in c.g.s. units. Accordingly he has, in most cases, been obliged to construct special types of apparatus adapted to the particular end in view. For obvious reasons, more attention has been paid to the requirements of the particular problems than to the physical principles and laws involved. Such limited, empirical methods of measurement in a very restricted field of investigation only make it difficult for workers in the same field in different countries to interpret the results of one another, and render it impossible to make any comparisons with results obtained in allied fields, such as the industry of artificial materials.

The fact that every physical investigation and improved technique must be based on a reliable and precise means of measuring the desired technical and physical properties has, fortunately, been given greater consideration of late by the rubber industry. The present author has been prompted by suggestions from various quarters¹ to study the special utility of the Höppler consistometer, developed by him, in testing raw materials, intermediate products, and finished products in the rubber industry.

The Höppler consistometer is an absolute consistometer, *i.e.*, the permanent state² of viscous, semi-solid and solid materials, which is governed by thermal, mechanical and time effects, and the behavior of these materials when subjected to a normal or shearing stress, is measured as a material constant, without the aid of empirical constants derived from the geometric dimensions of the instrument itself.

The results of the measurements are expressed in c.g.s. units, and it is possible to measure various properties, including viscosity, quasiviscosity, plasticity, flow point, η -flow point, the v/τ form of flow curve for purely viscous, quasiviscous, purely plastic, and quasiplastic materials, solidification flow, microflow, block flow, thixotropy, rheopexy, dilatancy, solidification phenomena, cone flow point (hardness), and, in addition to these, elasticity phenomena, such as spontaneous and secondary compression, spontaneous and secondary resilience, visco-elastic deformation, plasto-elastic deformation, thermal resilience, elastic hysteresis, etc.

The Höppler consistometer³ has already been described in detail elsewhere, so at this time only the principles involved in measurements by this technique will be described, and then only in a brief way. The apparatus (Figure 1) is equipped with the four mechanisms shown in Figure 1; I and II for rheologic, III for elastometric, and IV for cone flow point (hardness) determinations.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 17, No. 2, pages 17-23, February 1941.

Mechanism I.—A ball, carried by the guide-rod C in a hollow cylinder H, moves through the liquid material M under investigation, so that the liquid flows with a laminar motion through the concentric ring space between the ball and hollow cylinder. The ball is loaded by means of weights hung on a lever arm G in ball-bearings, and exerts a shearing stress of 0.125 to 60 kg. per sq. cm. on the liquid under flow. By means of a measuring device U connected mag-

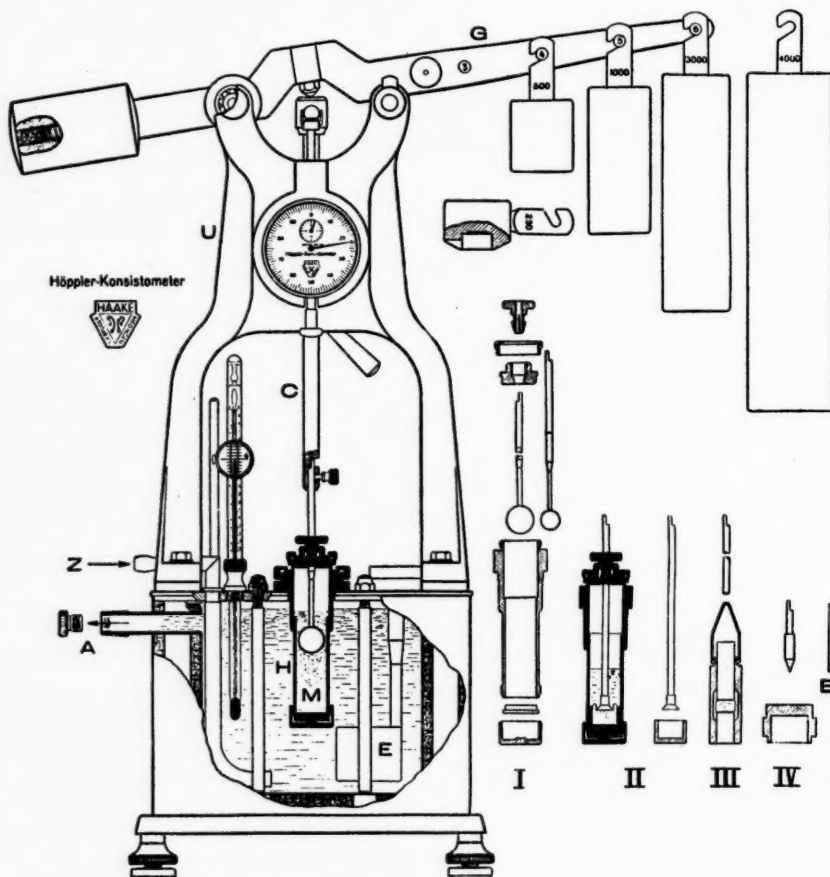


Fig. 1.

netically with the guide-rod, the movement of the ball and the average rate of flow of the liquid can be measured progressively within a range of 20 mm., with a precision of 0.002 mm.

Mechanism II.—The material under investigation is placed in a small container of 2-cc. capacity, and is deformed by a piston made up of a conical frustrum with a very sharply pointed base angle. In this case too, the material flows through a concentric circular space, under shearing stresses of 0.25 to 75 kg. per sq. cm.

Mechanism III.—The material is deformed between two pistons, each of 1 sq.

cm. (or 0.5 and 0.1 sq. cm.) cross-section, under loads from 0.25 to 50 (or to 750) kg. per sq. cm.

Mechanism IV.—A hard-metal ball of special design presses, under loads from 0.25 to 50 kg., as desired, into the material for a length of time or to a point at which the flow point for the part of the surface concerned is reached. The range of measurement is 1 to 50,000 kg. per sq. cm.

In the first experiments, an 18 per cent solution in a mixture of benzene and benzene (75:25) of 1a ribbed smoked sheet rubber, previously broken down on a mill for a short time, was studied at various temperatures and under various shearing stresses. In this case Mechanism I was used. Table I shows some typical results obtained at 20° C. When these results are shown in the form of a v/τ diagram, the flow curves in Figure 2 are obtained. From these curves,

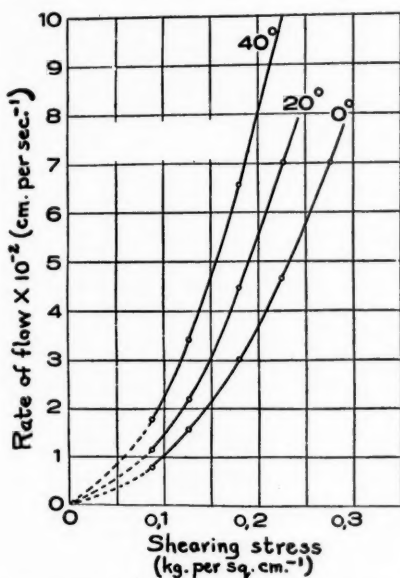


FIG. 2.—Fundamental viscosity of an 18 per cent rubber solution.

it is evident that the particular rubber solution studied exhibited quasiviscous flow. Since, when stored in a container, the solution showed a smooth, shining surface down to as low a temperature as 0° C. it could be classed, in the physical sense, as a liquid. Accordingly, it seemed justifiable to extrapolate the curve beyond the range of the experimental data (broken line in Figure 2) to the zero point.

The experimental results recorded in Table I and in Figure 2 represent the fundamental viscosity of the solution because, as was to be expected, the solution showed thixotropic properties. After homogenizing, it recovered its gel viscosity completely within two hours. The experimental values obtained in this case are recorded in Table II, and they bring out the interesting fact that, within the temperature range of 0° to 60° C studied, the thixotropy does not depend on the temperature, and averages about 9.6 per cent.

When the quasiviscosity of the rubber solution is calculated from the experi-

mental values of the rate of flow under the load applied (see Table I, last column), and this is plotted as a function of temperature in a coordinate system, the viscosity-temperature curves represented in Figure 3 are obtained. When a

TABLE I
MEASUREMENTS OF THE FUNDAMENTAL VISCOSITY OF AN EIGHTEEN PER CENT
RUBBER SOLUTION AT 20° C

G (g.)	τ (kg. per sq. cm.)	s (cm.)	t (sec.)	v (cm. per sec.)	η_0 (centipoises)
258	0.091	1	86.08	0.0116	126,400
358	0.126	1	45.40	0.0220	92,800
508	0.179	1	24.20	0.0414	70,100
708	0.285	1	9.85	0.1015	39,800

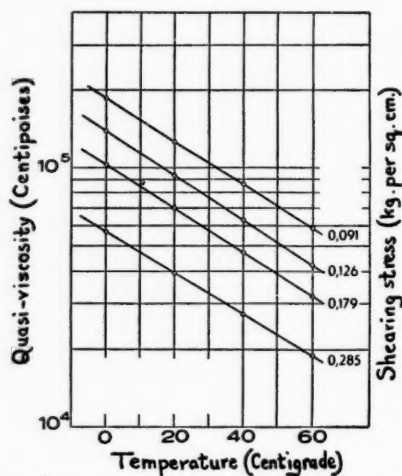


FIG. 3.—Fundamental viscosity of an 18 per cent rubber solution.

TABLE II
THIXOTROPY OF AN EIGHTEEN PER CENT RUBBER SOLUTION
($\tau = 0.091$ kg. per sq. cm.)

Temperature (°C)	Gel and fundamental viscosity	Rate of flow (v)	Thixotropy (percentage)
0°	Gel	0.00718	9.75
	Fundamental	0.00788	—
20°	Gel	0.01060	9.44
	Fundamental	0.01160	—
40°	Gel	0.01577	9.32
	Fundamental	0.01724	—
60°	Gel	0.02386	9.78
	Fundamental	0.02510	—

logarithmic scale is used on the η_0 axis, the surprising fact is observed that the curves become straight lines, and the various shearing stresses used in studying the solution are distinguishable merely by parallel displacements of these lines in the η_0/t diagram. Solutions of natural rubber and of artificial rubber products

of varying degrees of mastication and degradation can be distinguished at the same concentrations by the steepness of the straight lines. The intersection with the abscissa encloses an angle which can be utilized as a material constant.

Raw-rubber products are studied by Mechanism II. Preparation of a special test-sample is not necessary; rubber, *e.g.*, Buna, is cut in the raw state, without any particular treatment, by scissors, into pieces the size of corn or peas, and, by means of a hand-lever press or a sinter press (see Figure 4), is formed in three of four portions in the small measuring container A at room temperature.

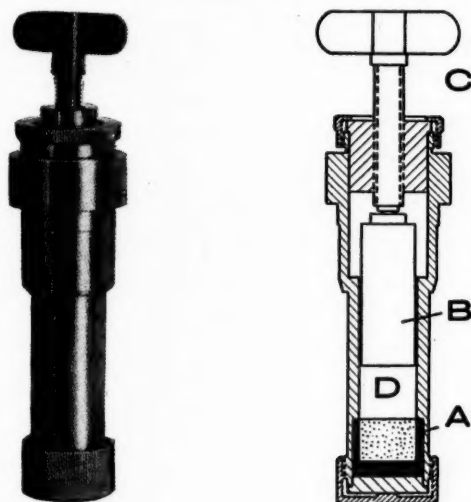


FIG. 4.

TABLE III
SMOKED SHEET MASTICATED 80 MINUTES
(Measurements made at 20° C)

G (grams)	τ (kg. per sq. cm.)	s (cm.)	t (sec.)	v (cm. per sec.)	$\frac{\eta_0}{cP}$
2,000	2	0	0	0	∞
4,000	4	0.015	468	0.000032	12.5×10^{10}
6,000	6	0.025	103.5	0.000242	2.48×10^{10}
8,000	8	0.05	83.1	0.000602	1.33×10^{10}
10,000	10	0.05	39.1	0.001280	0.78×10^{10}
11,000	11	0.10	56.6	0.001770	0.62×10^{10}

The initial elastic deformation brought about in this way plays no part in the results, since with this measuring device only plastic deformation is supposedly measured. After the measuring container is placed in the Höppler consistometer and the desired temperature is reached, the measurements can be started. The technique used in these measurements has been described in detail in the literature³.

To give sufficient time for elastic deformation, which precedes plastic deformation, to come to equilibrium, it is of advantage to begin with high shearing stresses. As a typical case, measurements, made at 20° C, of smoked sheet rubber masticated at 80° C, are shown in Table III. When the rates of flow v are plotted

on a coordinate system as a function of the shearing stress τ , the flow curve of the material is obtained. This curve is, in general, of the character shown in Figure 5. Within the range of shearing stresses A, the rubber still behaves as a solid body, *i.e.*, the shearing stress brings about only elastic deformation, with complete recovery to the original condition when the load is released. With increase in shearing stress, the rubber commences to flow, *i.e.*, it is deformed permanently. This point is termed the *flow point*. From the character of the flow curve, it is obvious that, within the range B, there is no proportionality between τ and v .

The shearing stress is not only spent in transmitting energy to the laminated layers which slide over one another, but also must perform further work, *e.g.*, the necessary preliminary work of orienting the extended micellar bonds of the rubber with their long axes parallel to the direction of flow. The energy necessary for this is manifest in a retention of the rate of flow. Region B is termed the range of *quasiplastic flow*.

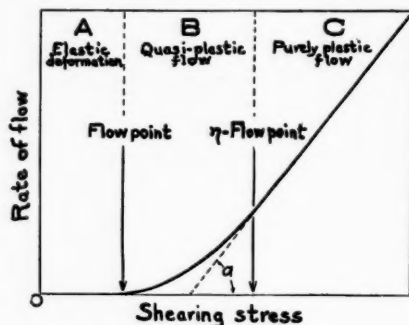


FIG. 5.—Flow curve.

With further increase in shearing stress and the accompanying increase in the rate of flow, the phenomena described disappear, *i.e.*, further deformation is linear from this point on, and the flow curve becomes coincident with its asymptote (see Figure 5). Since from this shearing stress on, η again becomes important as a proportionality constant, this point is designated as the η -flow point, and region C as purely plastic flow. Only in very highly plasticized or degraded rubber products, or under very high shearing stresses, does purely plastic flow take place.

The flow curves of eight rubber products are shown in Figure 6. It was, for example, observed that the higher the degree of mastication of smoked sheet, the nearer the flow curve and the flow point on the τ axis approach the zero point. If extrapolated in an approximate way by the trend of the curve, the flow point then becomes a straight-line function of the time of mastication (see flow-point curve, Figure 7):

To characterize a rubber product, it is not in the least necessary to follow the rather troublesome method of constructing a flow curve, although the time spent on doing this is only a fraction of that required, for example, at the beginning to make a Defo hardness determination. Actually it is necessary only to determine the velocity of flow, and with it the quasiviscosity η_0 at some particular shearing stress τ which depends on the conditions of the test. As an example,

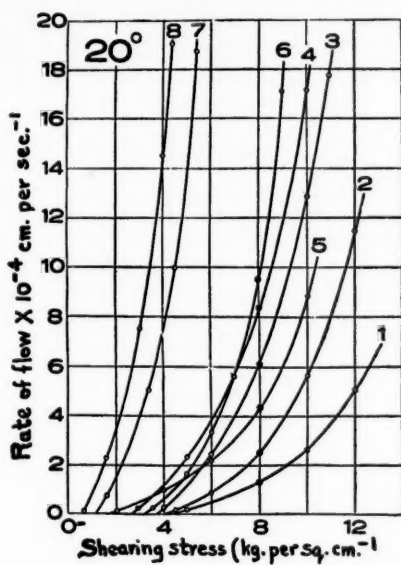


FIG. 6.

1. Smoked sheet masticated 40 min.
2. Smoked sheet masticated 60 min.
3. Smoked sheet masticated 80 min.
4. Smoked sheet masticated 120 min.
5. Buna-S maturated.
6. Buna-S thermally degraded.
7. Buna-S5.
8. Crepe dead-milled.

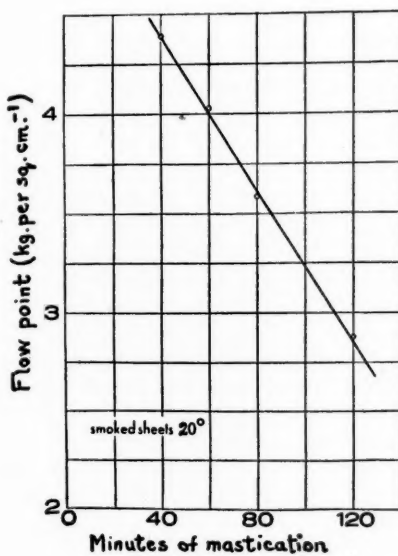


FIG. 7.

a τ value of 8 kg. per sq. cm. is shown in Figure 6, in which case, the rates of flow v of the first six rubbers lie within a range of 10 (represented by the black dots on the diagram). Since the elastic stresses must first come to equilibrium before the material shows purely plastic flow, only about one-half the load is applied at the beginning of the measurements, and only toward the end is the full shearing stress applied. It is extremely important to follow this procedure, in which case it is always sufficient to evaluate the measurements in the last part of the range (between 16 and 17 mm. on the scale). In this case a straight line on the s/t diagram is always obtained.

When the quasiviscosity η_Q values corresponding to the measured rates of flow are calculated, and these η_Q values are plotted as a logarithmic function of the temperature, this quasiviscosity-temperature relation is found to be a straight line. Different shearing stresses τ merely give other parallel straight

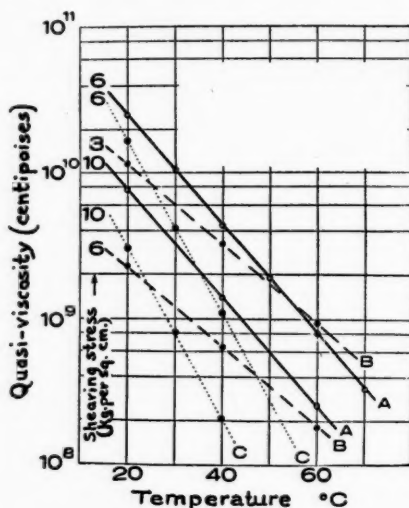


FIG. 8.

lines. Different raw rubber products are distinguishable by the different slopes of their straight lines (see Figure 8). Since this phenomenon had already been observed in the case of the rubber solution studied at the beginning, it may be assumed that this logarithmically linear course of the η_Q function is a property common to all rubber products, independent of the form in which they exist.

It is obvious that this method introduces a new and valuable material constant. The experimental procedure and the testing conditions have been worked out as follows. First of all, the raw rubber under investigation is moulded in the standard way in two small measuring containers of the Höppler consistometer. One of these containers is maintained at 20° C, the other container at 50° C, during the measurements. The same shearing stress is used in each case, *e.g.*, a stress between 3 and 6 kg. per sq. cm. It should again be mentioned that only a small preliminary stress is applied at first, so that the elasticity phenomena can come to equilibrium before the full shearing stress is applied to the rubber. With the rates of flow v (in cm. per sec.) measured at 20° C and at 50° C, and the values of the stress G (in grams) applied to the rubber, the quasiviscosity

values η_0 can be calculated (in centipoises) by the equation: $1000 G/v = \eta_0$. These values are then plotted on semilogarithmic paper, *e.g.*, on No. 396 $\frac{1}{2}$ paper of Schleicher and Schüll. Paper of this type is represented in Figure 9. Here the abscissa is a linear scale in mm., the ordinate a logarithmic scale covering four ten-power ranges, *i.e.*, from 10^7 to 10^{11} . The scale of the abscissa is such that 1 cm. corresponds to 5 Celsius degrees; each range of a ten-power on the ordinate corresponds to 25 degrees of temperature on the abscissa. Both points of measurement are then connected by a straight line, and the angle of slope of this straight line with the abscissa is read by means of a goniometer. The value obtained from this temperature-viscosity diagram is an important material constant, and is termed the *slope*.

In measurements of raw rubber and vulcanized rubber products, where the deformation is preponderantly elastic, Mechanism III is used. This principle

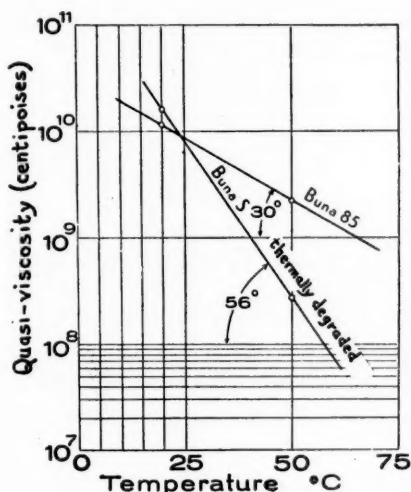


FIG. 9.

of measurement, *viz.*, observation of the behavior of a test-specimen which is compressed between two parallel plane surfaces is as old as are procedures for testing materials themselves⁴. In the elastometer device for use with the Höppler consistometer, this method of measurement is based strictly on scientific principles, and involves a special technique which utilizes the *c.g.s.* system.

The methods of measuring the coefficient of elasticity and modulus of elasticity, as well as the various types of deformation of a material, are described in detail in the reference already mentioned.³ A rubber technologist is interested above all else in that property of rubber which may be called its resistance to deformation.

If the phenomena which occur when a test-specimen is subjected to a compressive force are analyzed, the resulting deformation can be represented as in Figure 10. When a load is applied, immediate, spontaneous compression u takes place. This is followed by the after-effect v . When the load is removed, spontaneous recovery w takes place, followed by an after-effect x . Finally a permanent plastic deformation z remains.

The construction of a plasto-elastic deformation curve of this kind brings out the fact that a very long time is required for the after-effects v and x to become complete. In the case of rubber products, for example, these secondary effects are frequently appreciable even after several hours. However, since most of the compression and recovery take place within a period of a few seconds, it is possible to cut short the time required for their measurement (see Figure 11). If the testing conditions are suitably and clearly defined, it is possible to obtain quickly an important material constant, the *resistance to deformation* R which can be defined in the following way. This resistance to deformation R is the pressure in kg. per cm. necessary to compress a cylindrical test-specimen from

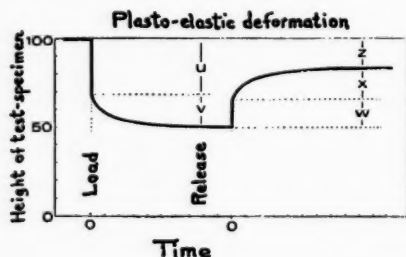


FIG. 10.

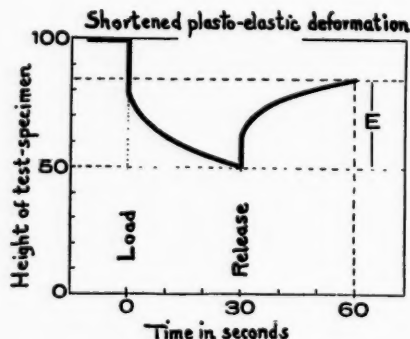


FIG. 11.

the height $h=d/2$ to $h=d$, between two surfaces conforming to its own diameter, at a temperature t to one-half its original height in a period of one minute.

In this case, deformation can be elastic, plastic, plasto-elastic or visco-elastic.

As a basis which can be used technically for measuring the elastic properties of a material, the amount E (see Figure 11) which the material recovers in the first minute after removal of the load is specified as the *elastic recovery* E , in percentage of the deformation; i.e., a test-specimen of height 100 which is compressed to height 50, and then recovers to a height of 75 one minute after removal of the compressive load, has an elastic recovery of 50 per cent. Since, up to 50 per cent deformation of the test-specimen, this relation is a linear one, it is possible to determine graphically the necessary compressive load. The investigator is therefore not ordinarily dependent on the results of experimental data, although there may be exceptions to this. The loads are plotted as abscissa

and the gauge readings as ordinate on millimeter paper (see Figure 12). In a representative case, the height of the test-specimen as measured was 9.840 mm.; the gauge reading, 11.202 mm. At 50 per cent deformation, the gauge reading would then be $11.202 + 9.840/2 = 16.122$ mm. At the beginning, a load was chosen which did not compress the test-specimen more than 50 per cent in 1 minute. It is advantageous to choose a load which is as close as possible to R . In the foregoing example, the test-specimen was subjected to a load of 15 kilograms; in this case the gauge reading was 14.800 mm. after 1 minute. This reading and

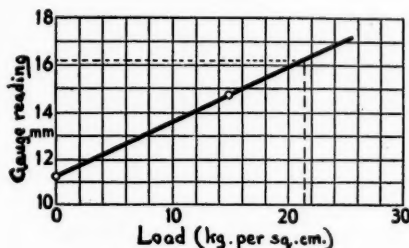


FIG. 12.

the reading of the gauge when no load was applied (11.202 mm.) were plotted on a coordinate system, and connected by a straight line. By graphic extrapolation, the load required to compress the test-specimen to a gauge reading of 16.122 mm. was estimated as 21.5 kg. per sq. cm. A second test-specimen was then measured under this same load and again the recovery one minute after removal of this load was measured. In the case cited, the gauge reading was 12.798 mm. Since the compression was $9.840/2 = 4.920$ mm., the elastic recovery R_{20} was $16.122 - 12.798 = 3.324$ mm. $= 100(3.324/4.920) = 68$ per cent. The resistance-to-compression and recovery values of a few vulcanizates are shown in Table IV.

TABLE IV

Vulcanizate	Resistance to deformation D_{20} (kg. per sq. cm.)	Elastic recovery R_{20} (percentage)
Soft Buna-S mix.....	7.12	97.8
Natural rubber mix.....	9.90	97.5
Natural rubber mix.....	13.9	98.1
Natural rubber mix.....	15.4	97.5
Buna-S mix	17.5	90.5
Leathery Buna-S mix containing a high proportion of reclaim.....	80.5	97.8

Socalled hard-rubber products, such as ebonite, should be tested by Mechanism IV, and the cone flow point measured, *i.e.*, the surface (in sq. cm.) is determined on which a given force (in kilograms) just brings about flow in the test-specimen. The theory and experimental technique of this method have already been described in detail³. The cone flow points of a few types of hard rubber containing various percentages of sulfur were found to be 3760 to 6100 kg. per sq. cm. at 20° C. The question frequently arises as to how rates of flow v or quasiviscosities η_0 , determined at a given shearing stress in the c.g.s. system by the Höppler consistometer, can be compared with measurements made by the conventional methods currently used in the rubber industry. In this connec-

tion it should be remarked that such a comparison appears quite possible if the expense is put into complicated mathematical apparatus and empirical constants are adopted. However, because of these complications, such a comparison would not seem to be of any practical value. As an example, the so-called Defo hardness may be cited. In compressing a test-specimen by the Defo method, a simple physical property is not measured, but rather a mixture of spontaneous compression and a compression after-effect, as well as plastic deformation. But even if these three types of deformation were to be combined

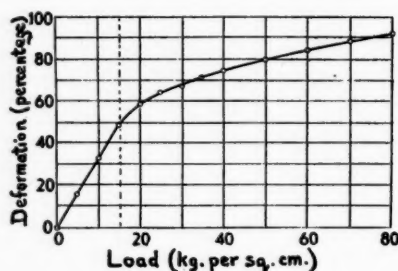


FIG. 13.

into a single property of technical value, equivalent in character to a stress, and could be expressed as the quotient of the load applied (in kilograms) and the cross-section (in sq. cm.), a further difficulty would be encountered, in that the Defo deformation curve follows only in part a linear course. This can be shown in a very simple manner experimentally by constructing an h/P diagram (see Figure 13) from measurements, preferably of a highly elastic vulcanizate. It is evident from Figure 13 that even the required Defo deformation of 60 per cent lies beyond the linear range. For this reason a maximum limit of 50 per cent was chosen in determining the resistance to deformation R .

TABLE V

Raw rubber	Treatment	Quasiviscosity (centipoises $\times 10^{10}$ at 20° C)	Defo hardness	Elastic component (percentage)
Smoked sheet	Masticated 40 min.	6.50	1050	21
Smoked sheet	Masticated 60 min.	3.31	725	17
Smoked sheet	Masticated 80 min.	1.31	600	15
Smoked sheet	Masticated 120 min.	0.96	425	11
Buna-S	Maturated	1.82	750	32
Buna-S	Degraded thermally	0.84	900	32

On the contrary, in the Höppler consistometer, purely plastic deformation is measured by Mechanism II, and elastic deformation by Mechanism III. Some comparative measurements are shown, by way of example, in Table V⁵.

It seems hardly necessary to call attention to the fact that it is unimportant and only time-consuming to work out a relation between a standard empirical method of measurement and another method based on the c.g.s. system. The specialist must decide upon one of the other methods of measurement at the very beginning of his work.

SUMMARY

A number of raw materials, intermediate products and finished products of the rubber industry were examined, and their rheologic and elastic properties measured by a Höppler consistometer.

The initial measurements were carried out with concentrated solutions of rubber and artificial rubber, and flow curves were constructed to show their behavior at various temperatures. The results show that the thixotropic properties of these materials are independent of the temperature. Also flow curves of solid raw rubber products of various degrees of mastication and at various temperatures were constructed and the corresponding quasiviscosity and flow point values were determined.

It was proved that the η_0/t function has a logarithmically linear course and, based on this fact, a new material constant is derived.

The elastic and plastic deformations of vulcanizates were studied experimentally on the basis of their resistance to deformation, and it is proposed that the hardness of hard-rubber products be measured and characterized by their cone flow points.

All measurements are based on the c.g.s. system.

REFERENCES

- ¹ The author was encouraged to carry out the present work by the editor of the journal *Kautschuk* and also by Dr. Hans Schmidt of Berlin. Dr. Ruthing of the Phönix A.-G., Harburg, and Dr. Weinbrenner of the Buna Werk at Schkopau, to whom thanks are due for furnishing the necessary samples.
- ² *Consistere* means to remain unchanged in any particular state.
- ³ Höppler, "Das Höppler-Konsistometer, Beschreibung, Anwendung und Handhabung, zugleich eine Einführung in die Systematik und Nomenklatur der Viskosimetrie, Plastometrie und Elastometrie," Fa. Gebr. Haake, Medingen b. Dresden, 1940.
- ⁴ Bauschinger 1876, Gulliver 1908, Sachs 1924, Karrer 1930, Scott 1931, Williams 1936, Houwink and Heinze 1938, Baader 1938.
- ⁵ The Defo measurements in this table were kindly offered, for use in this work, by Dr. E. Weinbrenner of Schkopau.

ELECTRICAL RESISTIVITY OF RUBBER COMPOUNDS *

J. G. ROBINSON

Although extensive published work is available on the general effects of the various rubber compounding ingredients on tensile strength, hardness, and other mechanical properties, the corresponding information for electrical resistivity is comparatively scanty. In the following work an attempt was made to develop

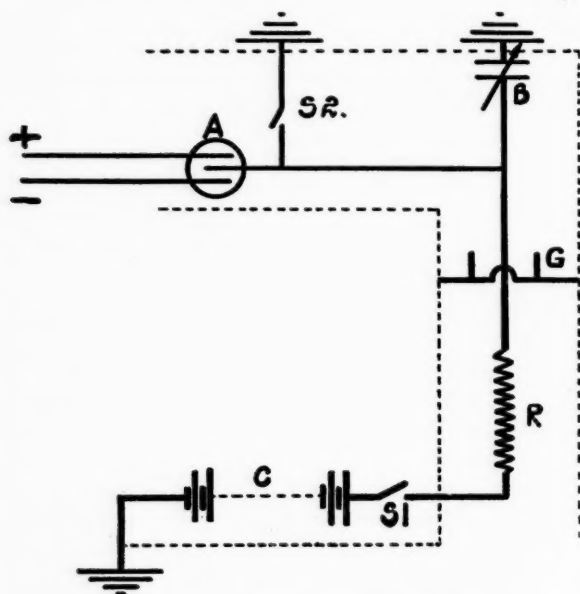


FIG. 1.—Circuit for rate of charge method.

- A Lindemann electrometer.
- B Calibrated variable air-condenser.
- R Unknown high resistance.
- G Earthed guard ring.
- C Source of high potential for application to R.
- S1 Switch in high potential circuit.
- S2 Earthing switch for electrometer.

Dotted lines represent an earthed screen.

a rapid and accurate technique for resistivity measurements with a view to obtaining data on a more extensive scale than previously reported.

Outline of method of test.—An electrometer method of measurement based on a paper by Church and Daynes¹ was used, but modifications were made, chiefly with respect to sample preparation and conditioning.

In this so-called "rate of charge" method (Figures 1 and 2), a definite voltage is applied to the specimen, which consists of a thin disc with painted Aquadag electrodes. The resultant leakage current is passed into an insulated system of

* Reprinted from *Transactions of the Rubber Industry*, Vol. 17, No. 1, pages 33-49, June 1941.

known capacity containing a Lindemann electrometer. The latter is a small electrostatic instrument, the deflection of which is directly proportional to the potential applied to its needle. At a given time after application of the voltage, the rate of deflection of the electrometer is directly proportional to the rate of increase of potential of the insulated system, which in turn is proportional to the leakage current at that time. This latter is inversely proportional to the resistance of the specimen; hence the latter may be calculated. Further details of the measurement, together with an example, are given in Appendix 1.

Extensive preliminary work was required to decide on the most suitable type of specimen and necessary conditioning treatment. It was found that, when a suitable specimen was exposed to air of a definite relative humidity, the resistivity

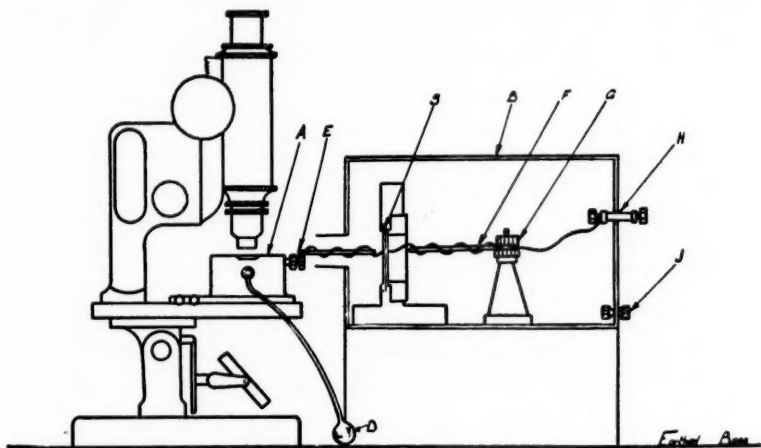


FIG. 2.—Test set up for resistivity measurements.

- A Lindemann electrometer.
- D Bulb for operating needle earthing switch of electrometer.
- E Needle terminal of electrometer, carrying rod and light spring to contact specimen.
- S Specimen, supported in wooden frame.
- B Box with hinged lid, lined with sheet aluminum and earthed by terminal J. Box is fitted with projecting aluminum tube continuous with lining to screen the connection between E and S.
- G Insulated stand carrying rod and spring F, in contact with the other side of the specimen.
- H Electrode for high-tension connection.

Connections to electrometer not shown in the diagram are: E to variable air-condenser; positive and negative leads to quadrant terminals; and earth connection to case.

eventually attained an equilibrium value characteristic of the compound and of the relative humidity chosen. This is parallel with the observation of Daynes² in relation to the water absorption of rubber compounds. The conditioning treatment was devised to ensure that the resistivity of the specimens had attained equilibrium with respect to air at 75 per cent relative humidity. Some notes on the development of the conditioning technique are given in Appendix 2.

All values of resistivity were measured one minute after application of the voltage, in conformity with usual practice.

Preparation of the specimens.—A stock of crude rubber and of compounding ingredients sufficient for an extended research was set aside and was used throughout. Mixings were made in the usual way on a 12-inch laboratory mill. The ingredients were not dried or treated in any way before mixing.

The rubber compound was calendered to 0.025 inch and rectangular pieces

were cut from portions of the sheet, selected for freedom from bubbles and other defects. These were cured in open steam, being supported on a sheet of aluminum and covered with a thin layer of French chalk.

Discs 5.6 cm. in diameter were cut from the vulcanized sheets, using a circular knife. The discs were cleaned by lightly rubbing with fine glasspaper. Electrodes were applied, using a watery suspension of deflocculated Acheson graphite, con-

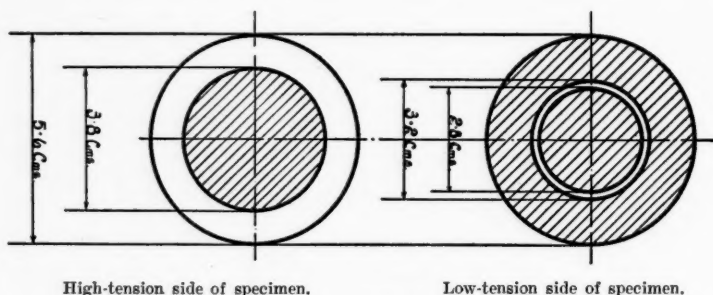


FIG. 3.—Electrode system.
Shading indicates graphited areas.

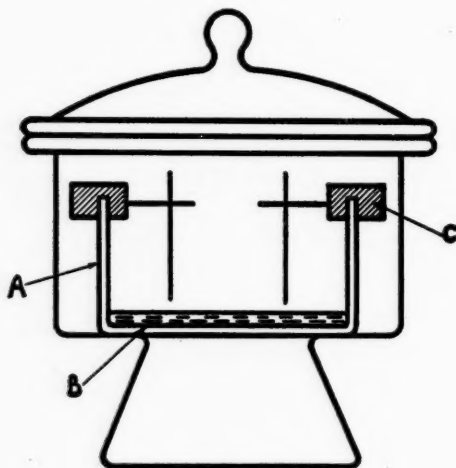


FIG. 4.—Humidifying chamber.
A Glass dish.
B Humidifying mixture.
C Slotted cork carrying specimens on pin.

sisting of 1 part Aquadag paste, 10 parts distilled water, by weight, with a little ammonia for stabilization. The electrode system is illustrated in Figure 3, and acknowledgments are made to the Research Association of British Rubber Manufacturers for suggesting this so-called "complete guard ring system of electrodes".

Specimens were gauged to the nearest 0.0005 inch using a Schopper screw micrometer with platens 1 cm. in diameter. Only one reading was made on each specimen, as it was found that there was no measurable variation over the small area of the electrodes.

Conditioning.—Specimens were transferred to a chamber illustrated in Figure 4 containing wet sodium chloride, giving a relative humidity of 75 per cent. Overcrowding of the specimens was avoided by putting a maximum of two specimens on each pin. The chamber was kept in a room the temperature of which was controlled at $70^{\circ}\text{F} \pm 5^{\circ}\text{F}$. The period of conditioning was 14 days, but occasionally a day or two longer was given to suit convenience in testing. It was shown (see Appendix 2) that under such conditions the resistivity of the specimens reach equilibrium with respect to air at 75 per cent relative humidity.

Testing technique.—Testing was carried out in a large room, the temperature of which was adjusted as near as possible to 70°F , and in most cases it did not differ by more than 2°F from this figure. The specimens were taken individually from the conditioning chamber for test, and replaced immediately after test. The testing operation was reduced to a smooth routine, so that an average of 24 specimens per hour could be tested. Exposure of the specimens to prevailing atmospheric conditions for this short period did not sensibly affect the resistivity.

TABLE I
VARIATION OF RATIO OF FRENCH CHALK TO ZINC OXIDE

Mix No.	1	2	3	4	5
Smoked sheet rubber.....	30.0	30.0	30.0	30.0	30.0
Pale crepe rubber.....	30.0	30.0	30.0	30.0	30.0
Sulfur	1.75	1.75	1.75	1.75	1.75
Mercaptobenzothiazole	0.3	0.3	0.3	0.3	0.3
Nonox-S	0.5	0.5	0.5	0.5	0.5
Zinc oxide	4.2	8.4	14.0	27.2	39.7
French chalk	25.0	22.9	20.0	13.3	6.9
Paraffin wax	2.0	2.0	2.0	2.0	2.0
Stearic acid	1.0	1.0	1.0	1.0	1.0
	94.75	96.85	99.55	106.05	112.15
Volume of zinc oxide in compounds (per cent)	1.0	2.0	3.35	6.5	9.5

Resistivity was calculated to 70°F , a suitable correction^a being applied for variation of room temperature from 70°F .

For each determination, four specimens were prepared and tested, and the results given are the mean of these four test-results. The consistency of the results obtained between different specimens of the same compound was excellent. The maximum variation of an individual sample from the mean was about 6 per cent.

EFFECT OF SOME COMPOUNDING VARIATIONS ON RESISTIVITY

The investigation was planned with the object of selecting the conditions necessary for the production of good class rubber compounds of high electrical resistivity. Consequently semi-conducting fillers, such as carbon black and low-grade compounding ingredients, were not considered. All experiments were made with compounds containing approximately 80 per cent by volume of rubber loaded with a mixture of French chalk and zinc oxide.

The compounds indicated in Table I contain 81 per cent by volume of rubber and 12.75 per cent by volume of mixed fillers. The accelerator, sulfur, anti-oxidant and softener ratios are constant, and the zinc oxide varies as shown.

Resistivity determinations over a range of cures are given in Table II.

It was evident that cure had only a small influence on resistivity, and the differences observed were due to the compounding variations. Zinc oxide concentrations up to 3.35 per cent gave no significant variation in resistivity, but beyond this point resistivity fell sharply with increase of zinc oxide concentration.

Variation of accelerator concentration.—In this and subsequent experiments, mixes were used which had for a base the following compound: smoked sheet rubber, 30 parts by weight; pale crepe rubber, 30 parts by weight; zinc oxide, 14 parts by weight, French chalk, 20 parts by weight, and paraffin wax 2 parts by weight, totalling 96 parts by weight.

Mercaptobenzothiazole (M.B.T.) was selected as the accelerator, and was used in three concentrations, shown in Table III.

Resistivity tests were made over a range of open steam cures at 30 lbs. per sq. in. In addition, and for comparison, tensile tests on Schopper rings and free

TABLE II
RESISTIVITY AT 70° F
(Unit, 1×10^{10} ohm-cm.)

Cure at 30 lbs. per sq. in. (min.)	Zinc oxide, per cent by volume				
	1.0	2.0	3.35	6.5	9.5
15.....	1.03	0.97	0.92	0.63	0.43
30.....	1.11	1.13	1.12	0.71	0.46
45.....	1.07	1.01	1.12	0.70	0.46
60.....	1.13	1.10	0.95	0.67	0.43

TABLE III

Compound No.	Additions to base mix			
	M.B.T.	Sulfur	Stearic acid	Nonox-S
6.....	0.3	1.75	1.0	0.5
7.....	0.6	1.75	1.0	0.5
8.....	0.9	1.75	1.0	0.5

sulfur determinations were made on press-cured slabs approximately 0.1 inch thick, using the same curing range. The free sulfur determinations were made by extracting with acetone, and oxidizing the extracts with bromine water. By subtracting free sulfur from that originally added, figures for combined sulfur were obtained. The results are given in Table IV.

The abstract in Table V was obtained by graphing the results in Table IV, and shows clearly the relation between tensile strength, combined sulfur and resistivity.

It is evident that resistivity reached a maximum at a cure somewhat less than that required for the attainment of maximum tensile strength, and that the value of resistivity decreased with increasing accelerator concentration. There was apparently no connection between maximum resistivity and combined sulfur.

Variation of Stearic Acid concentration.—The above experiments were repeated varying the amount of stearic acid, and details are given in Tables VI and VII.

It is evident that resistivity showed a progressive increase with increase of stearic acid concentration.

TABLE IV

Compound No.	Cure (min. at 30 lbs. per sq. in.)	Tensile strength (lb. per sq. in.)	Resistivity at 70° F (unit 1×10^{10} ohm-cm.)	Combined sulfur (parts per 100 rubber)
6	10	388	0.94	0.60
0.5 per cent M.B.T. on rubber	20	1940	1.05	0.75
	30	2340	1.06	0.91
	40	2585	1.16	1.25
	60	2690	1.01	1.75
7	10	1480	0.78	0.42
1.0 per cent M.B.T. on rubber	20	2525	0.85	1.09
	30	2820	0.91	1.42
	40	2775	0.92	1.75
	60	2540	0.94	2.37
8	10	2330	0.64	0.60
1.5 per cent M.B.T. on rubber	20	2755	0.75	1.42
	30	2770	0.60	2.09
	40	2560	0.53	2.25
	60	2435	0.66	2.59

TABLE V

Compound No.	Per cent M.B.T. on rubber	Time to reach maximum tensile (min.)	Time to reach maximum resistivity (min.)	Value of maximum resistivity	Combined sulfur for maximum resistivity
6.....	0.5	60	40	1.14	1.2
7.....	1.0	30	30	0.91	1.4
8.....	1.5	25	22	0.76	1.6

TABLE VI

Compound No.	Additions to base mix			
	M.B.T.	Sulfur	Stearic acid	Nonox-S
9.....	0.3	1.75	None	0.5
10.....	0.3	1.75	0.25	0.5
11.....	0.3	1.75	0.50	0.5
12.....	0.3	1.75	1.0	0.5

TABLE VII

RESISTIVITY AT 70° F
(Unit 1×10^{10} ohm-cm.)

Cure (min. at 30 lbs. per sq. in.)	Stearic acid (per cent)			
	None	0.25	0.50	1.0
15.....	0.34	0.60	0.71	0.92
30.....	0.56	0.86	0.85	1.12
45.....	0.73	0.85	1.02	1.12
60.....	0.77	0.96	0.92	0.95

Comparison of three antioxidants.—Similar experiments were made with three antioxidants. The proportions of antioxidant used were such as to give approximately equal protection against oxidation. Details are given in Tables VIII and IX.

V.G.B. and Nonox-S had little effect on resistivity, and Agerite-White caused a small decrease.

Comparison of accelerators.—Tests were made on a number of organic accelerators selected to include substances having diverse chemical structures and vulcanizing activity. The accelerators used were benzothiazyl disulfide (D.B.T.S.), zinc α -phenylbiguanide (Z.A.P.B.), diphenylguanidine (D.P.G.), *p*-nitroso-dimethylaniline (P.N.D.A.), and tetramethylthiuram disulfide (T.M.T.). The work was planned to bring out the effects of accelerator concentration, state of cure, and auxiliary materials, stearic acid, or calcined magnesia. When using tetramethylthiuram disulfide, the opportunity was taken to investigate two compounds containing no added free sulfur.

TABLE VIII

Compound No.	Additions to base mix				
	M.B.T.	Sulfur	Stearic acid	Benzidine	Antioxidant
13	0.375	1.75	0.75	0.0625	None
14	0.375	1.75	0.75	0.0625	Nonox-S 0.5
15	0.375	1.75	0.75	0.0625	V.G.B. 0.5
16	0.375	1.75	0.75	0.0625	Agerite-White 0.25

TABLE IX

RESISTIVITY AT 70° F

(Unit 1×10^{10} ohm-cm.)

Cure (min. at 30 lbs. per sq. in.)	No. 13 (no antioxidant)	No. 14 (Nonox-S)	No. 15 (V.G.B.)	No. 16 (Agerite-White)
15	0.91	0.95	0.84	0.76
30	1.11	1.14	1.12	0.86
60	1.00	1.08	1.05	0.87

In most cases, tensile tests on press-cured slabs, using the Schopper technique, were made, in addition to the resistivity tests. Details of the tensile tests are omitted in the interests of brevity, but the approximate time necessary to attain maximum tensile is indicated in the results, which are given in Tables X and XI.

The results in Table XI were considered in conjunction with those previously given for mercaptobenzothiazole in Tables IV, V and VII. Large differences in resistivity were produced by the various accelerators; for instance, in exactly comparable compounds, mercaptobenzothiazole (compound No. 9) gave values of the order of five times as great as diphenylguanidine (compound No. 25). The accelerators may be grouped in the following order of decreasing resistivity:

mercaptobenzothiazole	} about equal.
benzothiazyl disulfide	
zinc α -phenylbiguanide	
tetramethylthiuram disulfide	
<i>p</i> -nitroso-dimethylaniline	
diphenylguanidine	

TABLE X

Compound No.	Additions to base mix				
	Accelerator	Sulfur	Nonox-S	Stearic acid	Light calcined magnesia
17	D.B.T.S., 0.3	1.75	0.5	Nil	Nil
18	D.B.T.S., 0.6	1.75	0.5	Nil	Nil
19	D.B.T.S., 0.3	1.75	0.5	1.0	Nil
20	D.B.T.S., 0.6	1.75	0.5	1.0	Nil
21	Z.A.P.B., 0.3	1.75	0.5	Nil	Nil
22	Z.A.P.B., 0.6	1.75	0.5	Nil	Nil
23	Z.A.P.B., 0.3	1.75	0.5	Nil	1.0
24	Z.A.P.B., 0.6	1.75	0.5	Nil	1.0
25	D.P.G., 0.3	1.75	0.5	Nil	Nil
26	D.P.G., 0.6	1.75	0.5	Nil	Nil
27	P.N.D.A., 0.3	1.75	0.5	Nil	Nil
28	P.N.D.A., 0.6	1.75	0.5	Nil	Nil
29	T.M.T., 0.15	1.2	0.5	Nil	Nil
30	T.M.T., 0.15	1.2	0.5	1.0	Nil
31	T.M.T., 1.8	Nil	0.5	Nil	Nil
32	T.M.T., 1.8	Nil	0.5	1.0	Nil

TABLE XI

RESISTIVITY AT 70° F

(Unit 1×10^{10} ohm-cm.)

Cure		D.B.T.S. compounds			
Min.	Lbs. per sq. in.	17	18	19	20
15	30	0.21	0.33	0.63	0.44
30	30	0.25	0.36	0.70	0.69
45	30	0.58	0.48	0.77	0.70
60	30	0.68	0.48	0.65	0.73
		Z.A.P.B. compounds			
		21	22	23	24
15	30	0.13	0.20	0.47	0.33
30	30	0.29	0.36	0.47	0.34
45	30	0.46	0.48	—	0.35 *
60	30	0.66 *	0.65 *	0.36 *	0.36 *
		D.P.G. compounds		P.N.D.A. compounds	
		25	26	27	28
20	40	0.05	0.02	0.11	0.11
40	40	0.09 *	0.05 *	0.18	0.13
60	40	0.12 *	0.08	0.27	0.20 *
80	40	0.16	0.15	0.32 *	0.27
		T.M.T. compounds			
		29	30	31	32
10	20	0.40	0.77	—	—
20	20	0.56 *	0.76 *	—	—
30	20	0.68	0.62	—	—
40	20	0.70	0.65	—	—
10	30	—	—	0.10	0.48
20	30	—	—	0.10	0.31 *
40	30	—	—	0.14 *	0.37 *
60	30	—	—	0.22	0.58

* Cure or cures showing maximum tensile strength.

Some typical resistivity-time of cure curves are plotted in Figure 5, and it will be seen that, in absence of stearic acid and magnesia, the general tendency was for resistivity to increase throughout the curing range, and no change was observed in the region of maximum tensile strength. The sharp increase in resistivity shown by benzothiazyl disulfide (compounds Nos. 17 and 18) after the 30-minute cures is probably connected with the well-known delayed action of this accelerator.

Addition of stearic acid gave a general increase in maximum resistivity, accompanied by a marked modification of the resistivity-time of cure relationship. The curves generally had a form similar to the usual types of tensile strength-time of cure curves, but compound No. 32, containing no added free sulfur, was exceptional in that the curve showed a definite minimum about the middle of the curing range.

The addition of magnesia to the zinc α -phenylbiguanide compounds resulted in a decrease in maximum resistivity, accompanied by decreased variation of resistivity with cure.

Increase in accelerator concentration generally gave lower resistivity, and the effect was more marked with those accelerators giving high resistivity.

APPENDIX 1

DETAILS OF THE ELECTRICAL MEASUREMENTS

If R is the unknown resistance in ohms, V the applied voltage, S the sensitivity of the electrometer in scale divisions per volt, C the capacity in micro-microfarads of the insulated system containing the electrometer (*i.e.*, the electrometer, specimen, variable condenser and leads), and x the deflection of the electrometer in division after time t , then:

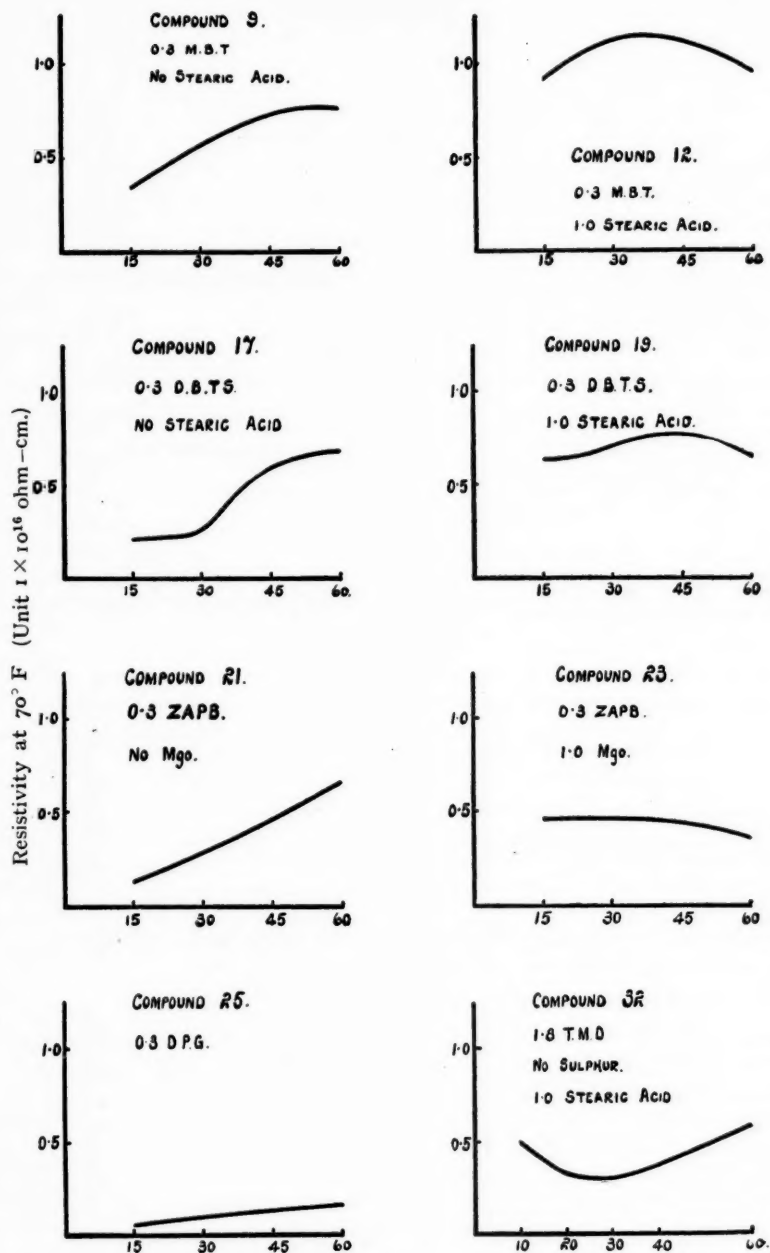
$$R = \frac{V.S. \times 10^{12}}{C} \div \frac{dx}{dt}.$$

To evaluate R , the observations required are, therefore: (1) voltage, read from a voltmeter, (2) sensitivity of the electrometer, obtained by applying a known voltage (up to 2 volts) and noting the steady deflection obtained, (3) capacity of insulated system, and (4) rate of needle deflection $\left(\frac{dx}{dt}\right)$ after time t .

The determination of items (3) and (4) is explained by an example given later.

The electrometer (see Figure 2) was mounted on an adjustable microscope stage and illuminated by transmitted light from the mirror. The movement of the needle was viewed through the microscope eyepiece, which was fitted with a micrometer scale. In setting up the electrometer, the quadrants and needle were first earthed, and the microscope stage manipulated so that the needle coincided with the centre of the eyepiece scale. Suitable voltages were then applied to the electrometer quadrants to give the required sensitivity. Increase of quadrant voltages gave a corresponding increase in sensitivity up to a point of instability. The positive and negative voltages for a given sensitivity were not equal, but one was adjusted in relation to the other so that the electrometer needle, when earthed, again coincided with the centre of the eyepiece scale. In other words, conditions were arranged so that the mechanical and electrical zero positions were the same.

To hold the specimens during test, a wooden frame on the principle of a photographic printing frame was used. The front and base of the frame were



Cure in minutes at a steam pressure of 30 lbs. per sq. in.

FIG. 5.—Types of resistivity-time of cure curves.

covered with a continuous sheet of aluminum, and the specimens were inserted so that the outer ring on the low tension side (Figure 3) made contact with the aluminum. As the latter was in contact with the earthed lining of the test box, the ring was effectively earthed. The central disc on the low tension side of the specimen was connected with the electrometer needle terminal E (Figure 2).

The connection between the electrometer needle terminal and the variable condenser was necessarily of low and constant capacity. After trials with various types of screened leads, a single piece of hard drawn copper wire was found to be quite suitable, provided precautions were taken to avoid hand capacity effects during testing.

In the early stages of the work, erratic and unstable behavior of the electrometer needle was experienced, and this was prevented by the simple expedient of storing the condenser, when not in use, in a closed box containing calcium chloride.

In testing a series of specimens, capacity determinations were first made on the whole series, followed by rate of deflection determinations. The procedure is illustrated by the following example.

For capacity determination, a specimen, prepared and conditioned as previously described, was inserted into the frame and placed in the test box B (Figure 2). Stand *G* was connected to earthed terminal *J*, thus earthing the electrode on the side of the specimen remote from the electrometer. With a capacity of 20 micro-microfarads in the variable condenser, the electrometer needle was charged to a potential of 2 volts by touching the needle terminal with the lead from a secondary cell, the other terminal of which was earthed. The deflection (30 divisions) was reduced to half this value by increasing the capacity in the variable condenser. The capacity reading in the latter was now 97 micro-microfarads. These readings enabled the capacity to be calculated as shown later.

For the rate-of-deflection determination, the specimen was inserted as for the capacity measurement, but stand *G* was connected to high-tension terminal *H* instead of earthed terminal *J* (Figure 2). The electrometer was earthed by compressing bulb *D*, and the high voltage switched on to terminal *H*. Simultaneously a stop-watch was started. After 50 seconds, bulb *D* was released, allow the insulated system to charge up with consequent deflection of the electrometer needle. Stop-watch readings were noted at regular intervals of the deflection, two observers being required.

Observations were also made of the capacity in the variable condenser, the high tension voltage and the sensitivity of the electrometer.

The following results were obtained:

Deflection of electrometer needle (divisions).....	0	5	10	15	20	25
Stop-watch readings, seconds.....	50	54	58	62	66	70

Capacity in condenser, 16 micro-microfarads.

Voltage, 205 volts.

Sensitivity, 15 scale divisions per volt.

Calculation.

Let C_1 be the capacity of the insulated system minus the capacity in the variable condenser.

Let C_2 be the initial capacity in the condenser.

Let C_3 be the capacity in the condenser required to reduce the initial deflection (and hence the original potential) to one half of its original value.

Then $C_1 = C_3 - 2C_2$.

Substituting, $C_1 = 97 - 40 = 57$ microfarads.

During the rate-of-deflection determination, the total capacity of the insulated system C was, therefore, $57 + 16 = 73$ micro-microfarads.

To evaluate $\frac{dx}{dt}$, deflection was plotted against time, giving a straight line,

from which it was deduced that $\frac{dx}{dt}$ at time 60 seconds was 1.25. In cases where a straight line was not obtained, the gradient of the tangent to the curve at time 60 seconds gave the value of dx/dt .

In the formula for calculating R , $V = 205$, $S = 15$, $C = 73$, $\frac{dx}{dt} = 1.25$. Also the thickness of the specimen was 0.025 inch, and the effective diameter of the electrodes 3.0 cm. The calculated resistivity was 3.75×10^{15} ohm-cm.

APPENDIX 2

DEVELOPMENT OF CONDITIONING TECHNIQUE

The first tests were made with specimens 0.15 inch thick, but it was found that these were quite unsuitable because the resistivity showed a progressive increase with storage, irrespective of the conditioning treatment. The examples in Table XII may be quoted.

TABLE XII

Compound No.	Additions to base mix				
	M.B.T.	Sulfur	Stearic acid	Nonox-S	Benzidine
14	0.375	1.75	0.75	0.5	0.0625
33	0.375	1.75	Nil	0.5	Nil

Sheets were cured for 25 minutes in open steam at 30 lbs. per sq. in., discs cut, and resistivities determined at various periods after cure. Between tests, the discs were stored at 70° F in a desiccator with a relative humidity of 75 per cent. The results are given in Table XIII.

Experiments were then made with much thinner (.025 inch) samples. These were exposed in desiccators, containing the following materials:

Phosphorus pentoxide giving 0 per cent relative humidity
 Wet sodium chloride giving 75 per cent relative humidity
 Wet potassium chloride giving 84.8 per cent relative humidity
 Wet potassium sulfate giving 97.2 per cent relative humidity

Inconsistencies and slow reaction to humidification were observed in the early experiments, and these were traced to incomplete exposure of the specimens to the humidifying agent. Adoption of the arrangement shown in Figure 4 and limitation of the number of specimens in the chamber gave much improved results. The thin specimens then showed a positive reaction to humidification, and for a given relative humidity an equilibrium resistivity was reached which was independent of previous conditioning. The figures were satisfactorily consistent from specimen to specimen and, for a given compound, were substantially reproducible.

The time taken to reach equilibrium depended on the type of compound, the relative humidity selected, and whether or not freshly vulcanized samples were involved. Thus, high-resistivity compounds took longer than low-resistivity compounds to reach equilibrium under all conditions. Freshly vulcanized compounds took much longer than compounds which had already been conditioned at another relative humidity.

TABLE XIII
RESISTIVITY AT 70° F
(Unit 1×10^{16} ohm-cm.)

Time of storage after cure	Compound	
	No. 14	No. 38
4 hours	1.07	0.33
6 hours	1.17	0.36
24 hours	1.29	0.49
2 days	1.31	0.42
3 days	1.24	0.47
4 days	1.35	0.50
5 days	1.46	0.54
6 days	1.19	0.54
7 days	1.43	0.54
9 days	1.85	0.74
12 days	2.29	0.84
13 days	2.05	0.97
40 days	2.92	1.36

TABLE XIV
RESISTIVITY AT 70° F
(Unit 1×10^{16} ohm-cm.)

Compound No.	Cure (min. at 30 lb. per sq. in.)	Relative humidity		
		0 per cent	75 per cent	97.2 per cent
14	15	2.72	0.95	0.65
	30	2.16(2.12)*	1.14(1.11)*	0.70(0.66)*
	60	2.32	1.12	0.78

* Figures in brackets represent an entirely fresh determination, using another batch of mixed compound.

The following were the maximum times found to be necessary to attain equilibrium when freshly vulcanized compounds were used.

Conditioned at 0 per cent relative humidity..... 7 days
Conditioned at 75 per cent relative humidity..... 14 days

When high resistivity compounds which had already reached equilibrium at one relative humidity were conditioned at another relative humidity, the time taken to attain equilibrium under the new conditions was approximately 2 days.

The results in Table 14 illustrate the variation of equilibrium resistivity with relative humidity, and also the reproducibility of results.

In the investigation of the effect of compounding variations on resistivity, it was obviously necessary to select one relative humidity at which all samples should be conditioned. As previously noted, 75 per cent relative humidity was selected, the reason being that it is the nearest in the range to normal atmospheric conditions.

SUMMARY

By means of a new technique for the determination of volume resistivity, the effect of compounding variations in a basic mixing containing about 80 per cent volume of rubber was investigated, with the following outstanding results:

(1) Above a certain limiting concentration, substitution of zinc oxide for French chalk gave decreased resistivity.

(2) Resistivity increased progressively with increase of stearic acid concentration.

(3) Of the three antioxidants examined, two had little effect on resistivity, one produced a decrease.

(4) The six accelerators examined produced large differences in resistivity; thus, mercaptobenzothiazole gave values of the order of five times that of diphenylguanidine.

(5) Increase in accelerator concentration gave decreased resistivity.

(6) The variation of resistivity with time of cure depended on the compound under investigation. The usual behavior was an increase with increased curing time, followed in some cases by a decrease. This is the same type of behavior which is shown by tensile strength, but no general connection could be traced between the development of tensile strength and of resistivity.

In conclusion, grateful acknowledgments are made to R. C. Milner for his valuable assistance in the experimental work.

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THE HEAT CONDUCTIVITY OF RUBBER AT LOW TEMPERATURES *

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INTRODUCTION

About a year ago I reported the results of some qualitative measurements of the heat conductivity of rubber at liquid-air temperature¹. The values at the low temperature turned out to be considerably smaller than at room temperature. I then wished to find out whether the heat conductivity decreased continuously from room to liquid-air temperature, or whether this drop was in any way connected with anomalies of other physical quantities occurring in the neighborhood of 200° K. At this temperature, for example, the specific-heat curve shows a sudden drop² and the specific-volume curve has a well defined kink³.

For this reason, heat-conductivity measurements were carried out to cover the intermediate region between liquid-air and room temperatures, the results of which experiments are the substance of this paper.

The cryostat used in this investigation is thought to be of a somewhat novel type and, at the same time, of rather simpler design than low-temperature thermostats previously described in the literature. As it may find application in other spheres of low-temperature research, it is described in detail. The actual heat-conductivity apparatus is a modification of that of Eucken⁴.

THE CRYOSTAT

The principle underlying this thermostat is to make and break, by manipulation outside the apparatus, a mechanical heat-contact between the cooling medium and the component or part which is to be maintained at an intermediate temperature. A cross-section of the arrangement is shown in Figure 1.

The vacuum enclosure 1 houses the device, and is evacuated through tube 2. The liquid-air container 3, suspended from the lid of vessel 1 by two tubes, is filled through one of them, the spout 4. The part marked 5 holds the conductivity apparatus inside the radiation screen 6, and it is this component which is to be kept at intermediate temperatures. Parts 5 and 3 are lined up with respect to each other and, at the same time, thermally insulated from each other by the short Perspex tube 7. Perspex is a poor heat conductor, which stands up well at low temperatures, and has been found most satisfactory.

Ignoring for the moment pin 12, heat contact between the liquid air in 3 and apparatus holder 5 is made through screw 8. This screw is worked by means of stem 9, which is brought out through tube 10 and packing gland 11 on top of it. This screw has a conical bottom fitting into a corresponding seating in 5. This gives a certain amount of self-centering. When the screw is turned down as far as it will go, heat contact is established, and the specimen cools down. As soon as the desired temperature is reached, the screw is loosened, and tightened again only at intervals to compensate for any rise in temperature due to radiation or heat generation inside the apparatus attached to 5.

* Reprinted from *The Proceedings of the Physical Society* (London), Vol. 53, Part 3, No. 297, pages 214-218, May 1, 1941.

A smoother working is achieved with the help of pin 12, which in effect is a variable heat resistance. Spring 13 presses the pin against the seating in 5, and this pressure and the free length of the pin protruding from the screw determine the conductance of the contact. By judicious initial adjustment, the temperature can be kept constant without interference for a considerable time.

It should not be difficult to make the device self-adjusting by appropriate electro-mechanical means.

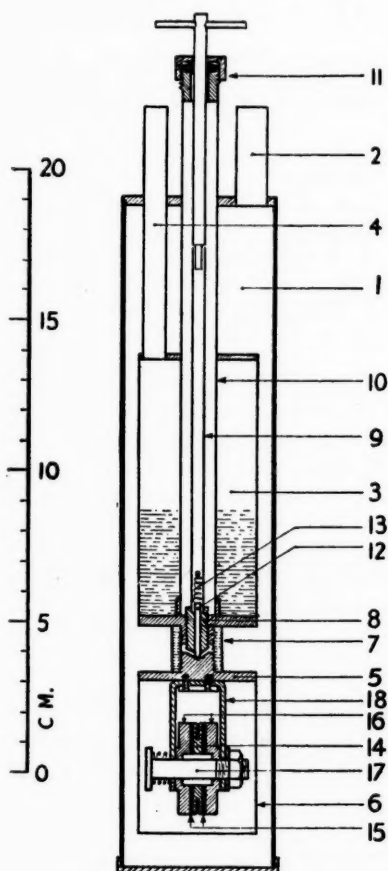


FIG. 1.—Cross-section of apparatus.

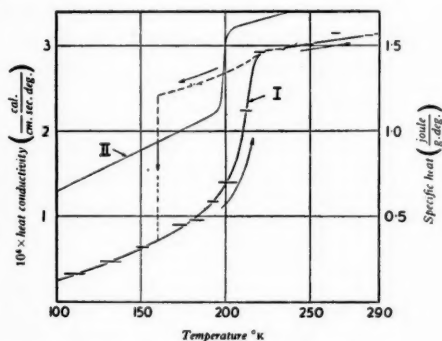


FIG. 2.—Thermal conductivity (I) and specific heat (II) of rubber⁶.

THE CONDUCTIVITY APPARATUS

The specimens have the form of flat rings of 30 mm. outside and 10 mm. inside diameter. The rings are punched out of sheet rubber. A heating element 14 is sandwiched between two such rings 15. The heating element is a flat copper reel, in the groove of which resistance wire has been wound. Two solid copper discs 16 cover the rubber rings on the outside, the whole being held together by the $\frac{1}{4}$ -inch nut and bolt 17. A stout spring shown on the left

side of the bolt ensures that the pressure on the rubber is maintained in spite of thermal contraction. The flexible laminated copper hoop 18, which is screwed to the discs 16 (screws not shown in the drawing), keeps these discs at the low temperature. The design is as symmetrical as possible to be sure of an equal heat flow from the heating element through the rubber discs.

The heat input is measured electrically with due regard to losses in instruments and leads. The temperature of the copper discs, which is the reference temperature of the measurement, and the temperature gradient across the rubber, are measured with copper-constantan thermocouples soldered flush into the faces of the disc and of the heating element.

We think that the contact resistances are not likely to falsify the results for the following reasons. A great number of experiments gave the same result within the limits of experimental error, and it is unlikely that the contact resistance was exactly reproduced under different experimental conditions. Apart from that, rubber gaskets used in vacuum work are found satisfactory, even at low temperatures, which fact rather proves that the rubber-metal contact is very good indeed.

Another doubt relates to the influence of copper on vulcanized rubber. It is well known that copper deteriorates rubber in the long run. The rubber discs used in our experiments showed a discolored surface after prolonged insertion in the apparatus, but otherwise there was no obvious change in the elastic properties, nor did fresh discs give different results from old ones.

RESULTS

The heat-conductivity measurements were carried out with North British cycle tube which is labelled as pure latex, electrodeposited; thus there are no fillers to be expected, apart from sulfur and accelerators. The results are shown in Figure 2, where the measurements are given as short horizontal lines, the lengths of which are equal to the actual temperature differences found across the rubber discs. Accordingly, the heat conductivity given by the ordinate of these lines is an average value in that range. The lines connected by the full thick curve I represent measurements made after having first cooled down the specimens to about 100° K. The reason for this procedure will be pointed out presently.

The heat conductivity rises steadily up to about 190° K. Near this temperature, the curve begins to rise more quickly, the maximum gradient being reached in the vicinity of 210° K. At 220° K, this sharp rise gives way again to a slow increase up to room temperature.

Whereas the low-temperature value is in fair agreement with our findings in the earlier experiments¹, the room-temperature value turns out to be much lower than that obtained previously. The reason for this discrepancy is to be found in the fact that the apparatus used before was not symmetrically constructed, so that the heat flow did not branch off equally through both discs.

If the measurements begin at room temperature, or any temperature above the second turning point of the curve I, the result is different. The heat conductivity declines comparatively little at first until it suddenly drops to a value on the ascending curve I, generally well below the first turning point of this curve. This behavior is indicated by the broken descending curve which, in contradistinction to the ascending curve, depends very much on the experimental conditions, mainly on the speed of cooling. Sometimes the temperature could be lowered as far as 100° K before the drop occurred. This critical point is easily

noticed without any measurements at all because it is accompanied by a clicking noise, which is probably familiar to anybody who has ever handled rubber in liquid air.

CONCLUSION

The experimental evidence points to the fact that a transition of some kind takes place at about 210° K, which, however, in consequence of supercooling, may take effect at a considerably lower temperature.

As is mentioned in the Introduction, there is other evidence of such a transition. The thin curve in Figure 2, which is taken from the paper of Bekkedahl and Matheson⁵, gives the specific heat of amorphous rubber. A sudden rise of this quantity occurs just below 200° K, and we feel sure that this near coincidence is more than accidental. The temperature lag between the two may be accounted for by the fact that Bekkedahl and Matheson worked with pure rubber hydrocarbon, whereas the material used for our investigation was vulcanized rubber. Bekkedahl's experiments³ on the temperature-volume relationship of various kinds of rubber showed that this transition is shifted towards higher temperatures when the rubber has been vulcanized.

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ELECTRICALLY CONDUCTING NEO-PRENE AND RUBBER *

B. J. HABGOOD and J. R. S. WARING

Introduction.—During the last decade great strides have been made in the fabrication of electrically conducting rubber. Such material has many useful applications, among which may be mentioned aeroplane and trolley bus tires, conveyor belts and flooring; in all cases the electrically conducting rubber helps to eliminate the effect of static electricity. Other applications for conducting rubber are found in the cable industry, as for example, conducting rubber compounds to replace metallic sheaths round the outside of the cables or actually as the conductor itself in place of metal.

The effect is usually obtained by loading the rubber with some form of conducting carbon, and the germ of the idea first appears in a patent applied for in 1929 by Bormann and Siemens Schuckertwerke A.-G.¹, who used carbon black and graphite in rubber. The patent deals specifically with the fabrication of an electric cable having conducting rubber next to the copper conductor and the prevent corona discharge in air pockets between the stranded conductor and the insulator. It was also suggested that a second conducting layer could be applied between the outside of the rubber insulation and the metal sheath.

In 1933, Granier² referred to the use of "oil black" to obtain conducting rubber vulcanizates, an equal weight of rubber and black being used. No particular technical effect appears to be obtained by the use of "oil black" instead of graphite or carbon black, a specific resistivity of 10^5 ohms per cm. cube being obtained, at a potential difference of 120 volts. The dielectric constant of the mixing was high, and radio applications were suggested.

During the next year or two, a number of application patents were taken out by Boggs and the Simplex Wire & Cable Co.³ and by Borel and the Société d'Exploitation des Câbles Electriques Système Berthoud, Borel et Cie.⁴

Boggs claims the use of rubber compounds containing upwards of 150 per cent of graphite on the rubber; the rubber compound is let down in solvent and spread on to fabric and then wrapped round the insulation to afford protection against corona cutting, the conducting rubber being either vulcanized or unvulcanized. Two typical formulas are given below:

	Parts by weight	Parts by weight
Smoked sheet	100	100
Graphite	233	275
Zinc oxide	5	5
Sulfur	2	2
Tetramethylthiuram disulfide	0.25	0.25
Antioxidant	—	1

Cure: 40 minutes at 260° F

Borel claims the use of conducting sheaths over the metal outer covering of cables to prevent electrolytic corrosion and, among the methods proposed, the use of gums such as rubber, balata, etc., to hold carbon particles in position,

* Reprinted from *Transactions of the Institution of the Rubber Industry*, Vol. 17, No. 1, pages 50-64, June 1941.

is mentioned. Graphite, charcoal and coke are suggested in addition to gas carbon as being satisfactory, and in all cases the major proportion of the covering consists of carbon.

The use of conducting rubber compounds for the protection of metal sheathed cables against electrolytic corrosion is dealt with by Jamey⁵, who describes the so-called electronic filter.

The Continental Gummiwerke A.-G. in its patents⁶ suggests the use of acetylene black for making conducting rubber, and the following is an example of the type of mixing employed.

	Parts by weight
Rubber	100
Acetylene black	100
Sulfur	3
Zinc oxide	15
Wood rosin	5
Stearic acid	1
Mercaptobenzothiazole	1

This mixing is not extruded, but is applied on a rubberized fabric.

Some interesting information is given in a paper by Heering⁷, who describes several applications of conducting rubber in the cable industry. A list of the specific insulation resistance of similarly prepared rubber compounds containing various types of carbon black is given, and it is shown that acetylene black is far superior to any of the other substances quoted. It is also pointed out that the use of conducting rubber sheaths helps considerably in protecting the cable against attack by corona discharge.

In another publication⁸, it is stated that the Dunlop Rubber Co. has developed a new technique which makes possible the production of electrically conducting rubber without the sacrifice of the normal properties of flexibility, abrasion resistance, etc., associated with earlier compounds based on graphite, lamp black, etc., but no details are given. It is, however, stated that rubber can be made with any required specific resistivity between the limits of 1 ohm and 10^{15} ohms, the latter being the specific resistivity of pure rubber itself. No information as to methods of measuring conductivity are given, particularly the voltage employed. As the conductivity varies with the voltage applied, the figures quoted give little indication of the utility of the compounds in actual service.

A patent by Bulgin and the Dunlop Rubber Co., Ltd.⁹, relates to the production of electrically conducting and fire-resistant articles comprised wholly or mainly of rubber, gutta-percha, balata or synthetic rubbers, such as Neoprene. It is pointed out that electrically conducting rubber compounds are likely to ignite when exposed to a current of high local intensity, due to excessive rise in temperature. According to the invention, a layer of electrically conducting rubber is applied to a layer of a relatively nonconducting flame-resistant rubber of at least equal thickness. Examples are given of electrically conducting rubber compounds which consist essentially of 60 per cent rubber with 28 per cent acetylene black, together with softeners, vulcanizing agents and antioxidants. It is clear that Neoprene compounds are of particular interest, owing to the inherent noninflammability of Neoprene itself.

Further patents on conducting rubber have been taken out by Reynolds and the Liverpool Electric Cable Co., Ltd.¹⁰, and by Morley, Scott and Webb and the Standard Telephones and Cables, Ltd.¹¹ The latter inventors claim the use of a conducting rubber strip combined with a sheet of plastic insulation by a

calendering operation. This compound strip is then applied to the conductor with the conducting layer in contact with it. The plastic insulation is applied thereto and the whole is vulcanized. The conducting rubber may consist of a mixture of 100 parts of rubber with 90 parts of acetylene black, and the plastic insulation may consist of a mixture of polystyrene with minor amounts of rubber, polyisobutene and vulcanizing ingredients. It is claimed that the use of a composite sheet prevents formation of voids between the conducting rubber and the plastic insulation.

Although it is clear that advances have been made in the technology of electrically conducting rubber, there is an almost complete absence of data in the literature. It nevertheless appears, from all the formulas produced in various patent examples and publications, that conducting materials cannot be readily extruded, and only in certain cases can they be calendered. Furthermore, in the case of compounds based on acetylene black, there is a considerable loss in conductivity after extrusion, coupled with development of anisotropy. Evidently, therefore, there is considerable room for more systematic work on electrically conducting rubber, not only from the technological angle of improving compounding, etc., but also to obtain actual data under known conditions and to standardize testing methods.

Theoretical.—The mechanism of electrical conduction in rubber is best explained by the assumption that leakage paths of carbon are formed throughout the rubber mass. These paths may be visualized as consisting of particles of carbon adhering together in the form of filaments, a phenomenon frequently encountered in colloid chemistry. On statistical grounds, reduction in particle size would be expected to increase the probability of filament formation, and this explains in a general way the improvements in electrically conducting rubber obtainable by using fine carbon blacks instead of those of large particle size, such as lamp black.

Variation in the conductivity with blacks of similar particle size must be attributed to a difference in the tendency to adhere and thus to form conducting chains. For example, gas black used in the rubber industry and acetylene black are similar in particle size, and are both considered to be reinforcing blacks. The electrical conductance of equally loaded rubber compounds are of a different order of magnitude and, furthermore, those compounds based on acetylene black have a greater tendency towards anisotropy. This anomalous behavior of acetylene black has been attributed to an elongated particle shape, but recent work carried out in America, using the electron microscope, seems to indicate that this may not be the case.

When it is remembered that all carbon blacks are made by controlled combustion of one form or another of combustible gas, and that the particular gas burnt must be chosen with care for the production of a channel black suitable for use in rubber, it is extremely likely that differences in the nature of the surface of the particle are at least as important as particle size and shape. It is therefore suggested that the observed anisotropic effects in rubber with acetylene black may be attributed to an anisotropy of the carbon black other than shape, for example, an asymmetric surface polarity. Such asymmetry would be expected to enhance the formation of conducting filaments.

Dispersion of the carbon black must play an important part in the resulting conductivity, as on adequate dispersion will depend the possibility of filament formation. In effect, a "bad dispersion" or agglomeration is equivalent to using a black of larger particle size. The term dispersion as used above has the mean-

ing in current use in rubber technology. If, however, it were possible to obtain an ideal dispersion, in which every particle of carbon black was enveloped in rubber, little or no conductivity would result. Developments in this direction have been achieved by the thermal after-treatment of mixings of carbon black and rubber and subsequent remilling. The dispersion of carbon black by such a process is so much improved that electrical conductivity is greatly reduced. This improvement in dispersion is also reflected in considerable changes in other physical properties, notably hardness and resilience.

In the conventional methods of processing, no heat treatment is applied between the mixing and vulcanizing processes, and the thermal treatment occurring during vulcanization causes changes similar to those referred to above. One of the authors of this paper (J.R.S.W.) has shown that the electrical conductivity of rubber carbon black compounds varies during cure¹² and this may be attributed to filament formation. It must be emphasized at this juncture that, although some filament formation takes place on the mill, the greater part takes place during the thermal treatment applied during vulcanization. The peptizing effect of accelerators on the rubber during this operation undoubtedly assists in the development of the conducting network of carbon particles.

It is clear from this discussion that, to obtain improved electrical conductivity, three possible lines of attack are open:

- (1) The use of very fine particle carbon blacks.
- (2) The use of fine particle carbon blacks in addition to acetylene black to reduce anisotropy.
- (3) Reduction of the viscosity of rubber before vulcanization to assist the development of conducting paths.

Experimental.—As stated above, the main difficulty in initiating work was the almost complete absence in the literature of data and methods of testing. For this reason it was necessary to carry out preliminary experimental work to set up standards and methods of evaluation.

In the course of investigations conducted several years ago in these laboratories into the mechanism of fatigue in rubber, it was found necessary to determine certain electrical characteristics of rubbers loaded with different types of carbon black, and it was noticed that materials containing large amounts of acetylene black were conducting and electrically anisotropic. For this reason all samples were prepared both as extruded tubes and as moulded sheets, and were measured for conductivity in both the longitudinal and the transverse directions. An experimental screw-type rubber extruding machine was employed, in which the shearing effect may be expected to be of a high order.

The dimensions of the tubes were, external diameter 8 to 9 mm., internal diameter 6 to 7 mm. About 10 feet of each mix was extruded, and samples about 35 cm. long were cut from each length for conductivity tests. The cured sheets were about 12 cm. square and 4 to 5 mm. thick. In all cases the measurements of dimensions were recorded. Sheets were wiped with acetone, and tubes were cleaned with a "pull-through" of dry cotton wool followed by second plug soaked in acetone.

Resistivity tests between the inside and outside of the tubes were carried out as follows: 30 cm. of the tube was bent double in the middle and immersed in mercury in a boiling tube, and the inside filled also. About one inch of tube projected at each end above the surface of the mercury. The current produced

by a potential difference of 6 volts between inside and outside mercury electrodes was measured with a galvanometer.

The current along the tube was measured on the same samples, so arranged that the ends dipped into two pools of mercury. A voltage of 120 volts was used, which on a 30 cm. length of tube gives an electric field of 4 volts per cm., which is somewhat smaller than in the previous case. A galvanometer with variable sensitivity was used for measuring the current.

Resistivity perpendicular to the plane of the sheet was measured, using standard E.R.A. mercury electrodes and guard ring, and the current through the sheet (with guard system) due to a 6-volt accumulator measured with a galvanometer. Resistivity along the sheet was obtained by using two large spring clips, 6.2 cm. wide and 7 cm. apart, applied to the edges of the sheets, the resistance being measured by means of a galvanometer and 9-volt battery. Before use the inside surfaces of the clips were cleaned with emery paper.

The measurements on transverse conductivity, both for tubes and sheets, are more reliable than those for the longitudinal conductivity. Reproducibility of tests on different samples of the same length of extruded tube was not good unless the second cleaning of the inside of the tube was done to remove last traces of French chalk.

Normally, test figures can be considered as having an accuracy of about 10 per cent. In every case the resistivity was calculated as a specific property from the dimensions of the sample. The values in the case of longitudinal resistivities of sheets are strictly comparable among themselves, although they may be in error from an absolute standpoint, due to the somewhat indefinite nature of the dimensions of the part tested.

These considerations refer to the electrical testing of samples of the same mix. If mixes of the same composition are made at different times, larger variations are introduced, due to differences in dispersion and in flow caused by variations in such factors as pressure or temperature. All these effects are particularly marked where there is any tendency to anisotropy.

In view of the lack of precise data which has already been referred to, the following mixings were made up to serve as standards.

RUBBER MIXINGS

	F.617	F.618
Rubber	100	100
Acetylene black	100	70
Tricresyl phosphate	20	15
Zinc oxide	5	5
Stearic acid	1	1
Sulfur	3	3
Mercaptobenzothiazole	1.25	1

NEOPRENE MIXINGS

	F.619	F.620
Neoprene Type E.....	100	100
Magnesia	10	10
Wood rosin	5	5
Tricresyl phosphate	15	12
Acetylene black	75	55
Zinc oxide	10	10

It was not possible to extrude mixes Nos. F.617 and 619 containing the higher volume loading of acetylene black. In Table I the electrical data are quoted.

The highly loaded mixes were hard, and tended to scorch in the extruder, and it was clear that, before tubes having a higher electrical conductivity could be obtained, the compounding would have to be altered to overcome the difficulties due to set-up. As it is well known that zinc oxide is the active curing ingredient of Neoprene and, further, that satisfactory vulcanization can be achieved by using magnesia alone, experiments were carried out with compounds containing no zinc oxide and, in addition, sheet balata was used as a plasticizer.

Comparison of the transverse and longitudinal resistivities of the extruded tube shows great electrical anisotropy. It was thought that the addition of a finer black might overcome the effect. The next mixes to be tested were, therefore, made up with a mixture of acetylene black and an extra-fine channel black (Kosmos F4) and, in addition, one experiment containing only Kosmos F4 was included. One rubber mixing was also made up containing mixed blacks,

TABLE I

Mix No.	Material	Acetylene black	Resistivity $\times 10^3$ ohms per cu. cm.			
			Tubes		Sheets	
			Through	Along	Through	Along
F.617	Rubber	100	—	—	0.31	0.01
F.618	Rubber	70	64	0.31	0.54	0.03
F.619	Neoprene	75	—	—	1.08	0.13
F.620	Neoprene	55	32	1.04	1.72	0.28

TABLE II

Mix No.	Material	Softener	Resistivity $\times 10^3$ ohms per cu. cm.						
			Blacks			Tubes		Sheets	
			Acet.	KF.4	Oxides	Through	Along	Through	Along
F.3590	Neoprene	12 TCP 10 Balata	40	15	MgO 10	100.0	43.0	10.0	2.9
3591	Rubber	15 TCP	50	20	ZnO 5	8.0	0.28	0.1	0.1
4400	Neoprene	15 TCP 10 Balata	53	22	MgO 10	9.4	2.2	0.15	0.2
4401	Neoprene	10 Balata	48	27	MgO 10	13.4	2.7	0.25	0.3
4402	Neoprene	10 Balata	58	27	MgO 10	3.0	1.2	0.18	0.15
5474	Neoprene	10 Balata	—	55	MgO 10	4.5	0.31	2.0	2.3

but no other variation in the compounding of the rubber stock was made. The relative compositions and the electrical characteristics of these compounds are given in Table II.

Comparing first the rubber composition No. F.3591 with F.618, it will be seen that the use of a mixture of acetylene black and extra fine channel black has reduced the electrical anisotropy to a considerable extent, both in the form of sheet and extruded tube. In addition, the resistivity has been reduced to a considerable extent, particularly in the through direction after extrusion.

In the case of the Neoprene compounds, a similar effect is observed and, in addition, it was found possible to extrude compounds containing as high as 85 parts of mixed carbon black. The extruded tube from mix F.5474 containing fine black alone was obtained only with difficulty, and was of poor quality.

Before proceeding further, it was thought advisable to see if the order of addition of the blacks had any effect on the electrical properties of the resulting compound. This was carried out only on Neoprene samples, which were tested in the form of extruded tubes.

It is clear from the figures above that it is advantageous to add the finer black first, and this order of addition was followed in subsequent experiments.

The reduction in electrical anisotropy and the reduction in loss of conductivity in the through direction after extrusion by the use of mixed blacks was sufficiently interesting to merit further investigation, and a few three-component systems were therefore examined, using Neoprene. The same basic formulas were employed, that is, the zinc oxide was omitted and balata included as a plasticizer. The first series was based on a mix containing 75 parts by weight of total black on 100 parts by weight of Neoprene. The results are given in Table IV.

The figures indicate that there is no great advantage in replacing part of the fine black by either similar quantities of a coarser black or by a still finer black.

TABLE III

Mix No.	Material	Acetylene black	KF4	Method of addition of black	Resistivity $\times 10^3$ ohms per cu. cm.	
					Through	Along
F.4207	Neoprene.....	53	22	Acetylene black first...	43	3.7
4207(a)	Neoprene.....	53	22	KF4 first	15	3.1
4207(b)	Neoprene.....	53	22	Together	43	5.0

TABLE IV

Mix No.	Blacks		Others	Resistivity $\times 10^3$ ohms per cu. cm.			
	Acetylene black	KF4		Tubes		Sheets	
				Through	Along	Through	Along
F.4948	53	22	—	21	1.4	1.0	0.25
4949	53	15	7 Kosmos T	39	4.4	3.5	0.3
4950	53	15	7 Kosmovar	25	3.0	0.9	0.5
4951	53	10	12 Lamp black	85	10.6	2.7	0.25

TABLE V

Mix No.	Blacks		Graphite	Resistivity $\times 10^3$ ohms per cu. cm.			
	Acetylene black	KF ₄		Tubes		Sheets	
				Through	Along	Through	Along
F.5209	58	27	—	1.6	0.24	0.29	0.1
5210	58	27	20	0.97	0.09	0.05	0.06
5211	48	27	30	1.24	0.11	0.12	0.07

Before finally dismissing the subject, it was thought advisable to examine the effect of graphite, as this material is widely referred to in earlier publications. In Table V the results obtained by using graphite as a third component are given, and it must be noted that the volume loading of these compounds is not constant, the graphite being added in addition to the quantity of carbon black in the best base mix so far obtained.

The figures show that improvements can be made by using 20 parts of graphite. It will be noticed that figures for the resistivity of mix F.4402 and F.5209, although repeats, vary to a considerable degree. This cannot be attributed to errors in testing the resistivity, but must be associated with difficulties in obtaining the same degree of dispersion in different experiments. This does not invalidate the conclusions obtained from any one series of experiments made up from mixes compounded at the same time. The improvements shown in the electrical properties of Neoprene in Table IV and V have been obtained by increasing

the plasticity of the Neoprene by the use of relatively large amounts of plasticizer, and it was thought that similar improvements could be obtained in the case of rubber. The use of highly peptized rubber naturally suggested itself, and it was considered that this method, used in conjunction with normal softeners, would aid the formation of conducting networks and would also enable much larger quantities of blacks to be used successfully, and thus allow higher conductivities to be obtained.

In the results quoted in Table VI, the rubber compounds are based on the following formula:

Peptized rubber	100
Carbon black	70-100
Tricresyl phosphate	15
Balata	12
Zinc oxide	5
Stearic acid	1
Sulfur	3
Mercaptobenzothiazole	1

The rubber was peptized by adding 1 per cent of Vulcamel to the rubber, which was then milled at 95° C for 30 minutes.

TABLE VI

Mix No.	Blacks		Graphite	Resistivity $\times 10^3$ ohm per cu. cm.			
	Acetylene black	KF4		Tubes		Sheets	
				Through	Along	Through	Along
F.5475	—	70	—	1.10	0.06	0.61	0.26
5700	—	70	—	0.28	0.06	0.05	0.08
5701	100	—	—	0.32	0.12	0.11	0.02
5702	70	30	—	0.38	0.13	0.06	0.05
5703	50	20	20	0.6	0.17	0.18	0.08

A study of the figures quoted above shows that the use of peptized rubber enables materials having a good conductivity in the through direction to be obtained. In addition, the extrusion of the compound is helped very considerably, and the finish of the extruded tube is excellent, even where loadings of 100 parts of black on 100 parts of peptized rubber are employed, *e.g.*, mix No. F.5475 made from unpeptized rubber gave a rough surface, whereas mix F.5700 gave an excellent finish.

The reduction in electrical anisotropy brought about by the use of peptized rubber is considerable, the anisotropy factor for tubes being reduced from 18 to 5 (compare the figures for mixes F.5475 and F.5700 in Table VI).

The correct choice of accelerator is important to obtain the maximum peptization over a period of time sufficient to allow of the formation of a conducting network. For example, thiocarbanilide, which starts curing immediately, gives less conducting compounds than other accelerators such as mercaptobenzothiazole.

If the stresses and particularly the high shear induced on the rubber in the screw driven extrusion machine used for the preparation of the tubes are considered, it becomes clear that the more liquid characteristics of the peptized materials help to relieve the strains set up during extrusion. The effect of shear is likely to be less pronounced on larger machines, where a longer time of recovery between the screw and the die is available. Temperature has an important effect on recovery time. In the experiments described in this paper, extrusion was carried out between 60° and 65° C.

A further interesting point arises out of this series of experiments, namely, that an equivalent electrical conductivity can be obtained by the use of 70 parts of fine black alone, as opposed to 100 parts of acetylene black alone or in mixtures. A number of experiments was also carried out in which quantities of various metallic powders were added to the blacks, but the results were so disappointing that this line was abandoned.

An examination of Table 6 shows that an electrical resistivity of about 300 ohms per cu. cm. in the through direction can be obtained, either by the use of 100 parts of acetylene black alone, or by 70 parts of Kosmos F4 alone, or by a mixture of these two blacks. These three mixings were evaluated by standard testing methods, and the results are given in Table VII.

Although no resilience figures were obtained for the compound containing F4 black alone, it is clear from results obtained from the mixture that acetylene black gives a more resilient product of lower tensile.

TABLE VII

	F.5700 (KF.4)	F.5701 (acet.)	F.5702 (mixture)
Tensile strength (kg. per sq. cm.)	142	111	114
Elongation (per cent)	585	190	253
Hardness (Shore)	66	79	72
Elasticity (Shore)	36	33	36
Compression set (per cent)	2	1	2
Resilience	—	72.8	35.0
Indentation	—	8.3	9.8
Swelling in Diesel oil at 70° C (7 days) (per cent)	320	192	226

TABLE VIII

	F.5210	F.5709
Tensile (kg. per sq. cm.)	170	—
Elongation (per cent)	127	—
Hardness (Shore)	92	94
Compression set (per cent)	16	13
22 hrs. at 70° C, 45 lbs. per sq. in.	1	2
Swelling in Diesel oil at 70° C (7 days) (per cent)	35	31

The improvements in electrical properties, and particularly the reduction of anisotropy, brought about by the use of highly peptized rubber made it necessary to examine the use of peptized Neoprene. It should be noted that Vulcamel will not peptize Neoprene, but that Neoprene Type G, etc., can be plasticized by the addition of guanidines and certain other accelerators.

The following mixing was prepared:

	F.5709
Peptized Neoprene	100
Sheet balata	10
Tricresyl phosphate	12
Wood rosin	5
Acetylene black	48
Kosmos F4	40
Graphite	20
Light calcined magnesia	10

After extrusion and vulcanization, a transverse volume resistivity of 0.320 ohm per cu. cm. and a longitudinal volume resistivity of 70 ohms per cu. cm. were obtained. The mechanical properties of Neoprene mixings Nos. F.5210 and F.5709 are given in Table VIII.

Resilience was not determined, owing to the relative hardness of the materials. Elasticity figures (Shore) are low.

For many purposes resilience is of no particular consequence, particularly when it is remembered that deformation sufficient to cause a moderate extension of the rubber causes a rapid loss of conductivity¹³. For this reason electrical conducting materials based on Neoprene have one important advantage, namely, that they are not swollen by oils, etc., to anything like the same extent as is rubber and, therefore, are less likely to lose their conductivity so quickly or to such a large extent in service conditions where oil is encountered.

Applications.—It is necessary to consider at this juncture the uses of electrically conducting materials in somewhat greater detail. There are two main fields where such material might find application, namely, for the dispersion of static electricity, and for the protection of cables, etc., that is, as a replacement for the lead sheathing. Here there is a dearth of information on the specification side, in just the same way as there is a comparative absence of data on the testing side, but a recent paper by Jevé¹⁴ gives a general survey of present-day uses for preventing accumulation of static electricity, and the use of semi-conducting rubber in motor cars is treated in a paper by the Rubber Manufacturers, Inc.¹⁵

It seems likely, that, for the dispersion of the usual voltages encountered in static electricity, a resistivity of the order of 10^6 ohms per cu. cm. will be sufficient. In this case, almost any of the compounds referred to in this paper will be equally satisfactory, and the selection of any one will depend on the ease of processing, the mechanical properties, the effect of swelling and so on. The subject of static electricity in industry is fully treated in a paper by Guest¹⁶.

For aircraft tires, resilience is of primary importance, and loading with black must be kept down to reasonable limits from this point of view. At the same time, owing to the detrimental effect of stretch and deformation on conductivity, a resistivity lower than 10^6 ohms per cu. cm. might be necessary to have a sufficiently large factor of safety.

In a paper by Law¹⁷, mention is made of a conducting rubber tire having a specific resistance of 50 ohms, compared with 5×10^7 ohms for a standard rubber tread, but no details are given with regard to processing or testing. The use of such highly conducting tires is claimed largely for combating current discharge on electrically-operated trolley buses.

For belting, resilience is not so important, although the effect of deformation may be of the same order as for tires. Flooring presents but little difficulty, as it is not subject to repeated flexing, although in certain cases oil resistance may be of importance.

At first sight it would appear that, as far as the second field of application is concerned, the idea of replacing lead sheathing with a semiconducting rubber or plastic semiconductor would require so much fundamental development work on the electrical side as to be worth while only if certain other outstanding advantages are to accrue. When it is remembered, however, that in multiple conductor cables of small diameter, from 50 to 60 per cent of the weight is due to the lead sheathing and that, even in the case of large diameter cables, the lead constitutes from 30 to 33 per cent of the weight, it becomes clear that there is a definite field for application of a light material having sufficiently good electrical properties. In a paper by Breitenstein¹⁸, the use of synthetic materials as covering for ships' cables is considered in great detail, and it is pointed out

that the substitution of lead by other material in ships, and particularly in battleships, is of tremendous advantage in saving in total displacement.

The best conducting rubber claimed in the literature has a resistivity of 1 ohm per cu. cm.¹⁹, *i.e.*, a conductivity at least 50,000 times less than that of lead, and it is clear that, in the event of an electrical breakdown, conditions might easily be met where the flow of current would be sufficiently great to heat up the rubber above ignition temperature, owing to the poor thermal conductivity of the rubber. Furthermore, as the voltage increases this possibility becomes much greater. It would seem, however, that if a metal braid, or tape were applied in intimate contact with the conducting layer of sheathing, or if the outer surface were plated with metal, this possibility would be greatly diminished. In any case some protective system would be necessary in most cases to prevent mechanical damage to the sheath. Jevé¹⁴ has pointed out the importance of good electrical contact with the more conducting compounds, and the use of a conducting paint on the surface of conducting rubber is recommended.

It would appear necessary to make the conducting sheathing as flame-resistant as possible, either by the use of a double compound, such as is claimed by Bulgin and the Dunlop Rubber Co.⁹ or by the use of a single compound containing fireproofing ingredients in addition to carbon black. Neoprene, of course, lends itself to the production of fire-resistant compounds, owing to its relatively high halogen content.

It has already been shown that polythene, which is an outstanding electrical insulator, can be rendered electrically conducting by the addition of carbon black²⁰. The use of other plastics naturally suggests itself in this connection, and the whole subject is under investigation.

Plasticized polyvinyl chloride is a noninflammable plastic, which would lend itself to the production of electrically conducting nonflam products.

It is clear that much work still remains to be done in the field of electrically conducting rubberlike materials and plastics and that, as improvements are made, the sphere of useful application of such products will be largely increased.

SUMMARY

- (1) The scattered references in the literature dealing with conducting rubber have been collected together.
- (2) A résumé of existing ideas on the mechanism of electrical conduction is given, from which certain lines of development work suggested themselves.
- (3) Electrically conducting Neoprene or rubber compounds based on acetylene black are anisotropic, an effect which is particularly pronounced after extrusion.
- (4) By the use of fine channel black, either alone or in addition to acetylene black, the transverse conductivity is improved, thus reducing the anisotropy.
- (5) A further improvement can be obtained by using highly plasticized Neoprene or rubber which reduces the shear during extrusion operations. In the case of Neoprene, zinc oxide is omitted from the mixings to prevent set-up.
- (6) Conducting tubes having a transverse volume resistivity of 300 ohms per cu. cm., and a longitudinal resistivity of 60 to 70 ohms per cu. cm. have been obtained, using a potential difference of 6 volts.
- (7) Provisional methods of testing conducting rubber are suggested.

In conclusion, the authors wish to express their thanks to Imperial Chemical Industries, Limited, in whose Rubber Service Laboratories the work was conducted, for permission to publish the results embodied in this paper.

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A TORSIONAL HYSTERESIS TEST FOR RUBBER

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The authors of the paper on "A Torsional Hysteresis Test for Rubber", which was published in the January 1941 issue of RUBBER CHEMISTRY AND TECHNOLOGY, pages 35-44, wish to correct two errors.

On page 40, under Equation (8), a is defined as the cut thickness of the test-piece, and b as the cut width of the test-piece (width of die).

Actually a should be defined as one-half the cut thickness of the test-piece, and b as one-half the cut width of the test-piece (width of die).

THE STANDARDIZATION OF RUBBER FLEXING TESTS *

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The present paper offers a method for standardizing rubber breakdown tests which is an adaptation of discriminant function analysis recently developed by R. A. Fisher, and hitherto applied only to the treatment of biological data.

The data which form the subject of the present study are rather inadequate, but it is worth while to use them to make the method available for more extensive investigations at a later date. It has, at least, revealed a gross lack of control

TABLE I
DATA FOR TWENTY FLEXING TESTS ON RUBBER

First Test										Total Number of Flexings	Second Test									
1	2	3	4	5	6	7	8	9	10		1	2	3	4	5	6	7	8	9	10
										4,500										
										9,000										
										13,500										
										22,500										
										31,500										
										40,500										
										49,500										
										58,500										
										67,500										
										85,500										
										103,500										
										121,500										
										139,500										
										157,500										
										175,500										
										193,500										
										211,500										
										229,500										
										247,500										
										265,500										
										283,500										
										301,500										
										319,500										
										337,500										
										355,500										
										373,500										
										391,500										
										409,500										

The progressive deterioration scores are denoted by letters A to K, with I excluded. Italic letters denote complete rupture of test-piece.

in experimental technique, and shows that great improvements must be made on the practical side to give the new statistical method a chance to show its real sensitivity.

1. TESTS AND DATA

Samples of ten different kinds of rubber were "bend-flexed" by a De Mattia machine. At suitable intervals the machine was stopped, and the state of breakdown of the rubber rated qualitatively by comparison with a series of pieces showing successive stages of breakdown. The whole was repeated with a second sample of each of the ten kinds. Originally there were ten qualitative scores, but an inspection of the data (Table I) showed that there was no point in discriminating between the advanced stages of disintegration at which different samples were able to hang on indefinitely, as, for example, Nos. 4 and 5 at K and No. 9 at H. These represent such extreme stages of breakdown (the rubber being broken through the middle) that, both for practical and statistical reasons, the test

* Reprinted from the *India Rubber World*, Vol. 102, No. 5, pages 36-41, August 1, 1940.

should be regarded as definitely finished as if the rubber had broken completely in half.

We therefore decided that the relevant data should be the more moderate stages of breakdown represented by the first five letters, A-E, although possibly F and G could also have been included.

The first attempt to apply the methods explained below also showed that rubber 8 was very anomalous and, if included, would necessitate much elaboration of the statistical method and destroy the simplicity of the results. It is, of course, obvious from the qualitative data that 8 on both occasions was very weak, since it had already reached stage B at the first observation. Since this was only a preliminary investigation, we felt justified in discarding the two tests of No. 8 from our data. It is very likely that the comparatively simple method which is then possible will be adequate for comparison of all rubbers which are not too widely different in flexing resistance, *i. e.*, for all comparisons which one would want to undertake in practice.

Alternatively, if the assumptions do prove to be inadequate, the statistical method can, without great difficulty, be elaborated to deal with a more complex situation.

2. SCALING THE NUMBER OF FLEXINGS

On looking at the original data, we see that in different rubbers the progress of breakdown differs in at least two respects. Firstly, the initial (or the mean) breakdown point may be early or late; secondly, the time taken to pass from the initial stage A to the "final" stage E may be short or long. On the face of it, it seems that two parameters (at least) would be required to specify the behavior of the rubber. This may indeed be theoretically necessary, but any device which would in practice specify the flexing resistance of the rubber by a single parameter, without doing violence to the data, would be extremely welcome.

Noting, for example, that in the first set of tests, No. 1 begins (A) at 67,500 and finishes (E) at 247,500, whereas No. 5 takes from 9,000 to 31,500 for the same process, we are led to the idea of transforming the scale of number of flexings to a scale of logarithms. This device would suggest itself even more forcibly to those who know the success of the same method in other fields; for example, in toxicology, where poison strengths, for statistical purposes, should usually be measured in logarithms, and in physiology where responses are in arithmetic progression, to stimuli which are in geometrical progression.

We therefore took, as our measure of the treatment to which the test-piece had been subjected, the common logarithm of the number of flexings $\div 1000$, as is shown in Table 2. After this had been done, it was, of course, necessary to test the truth of this assumption. If the transformation is successful, we expect to find that the test-pieces continue to differ from each other in their mean breakdown points, but no longer differ in their rates of breakdown.

3. SCORING THE QUALITATIVE OBSERVATIONS

3.1. Except for the fact that the letters represent successive stages of breakdown, we have absolutely no *a priori* idea of how these letters stand on a quantitative scale. For example, is the "distance" between A and B more or less than the "distance" between D and E? The answer is that the data themselves must determine the quantitative scores. Since the treatment is measured by log flexings, it is clear that the letters should be so scored that the state of breakdown is linearly related to log flexings. Moreover, since we have assumed that on the

log scale the rates of breakdown are the same for all tests, we must so allocate the scores to give minimum deviation from a set of regression lines, which have a common slope for all tests, but different positions for different tests (See Fig-

TABLE II
QUALITATIVE DATA AND MARGINAL TOTALS

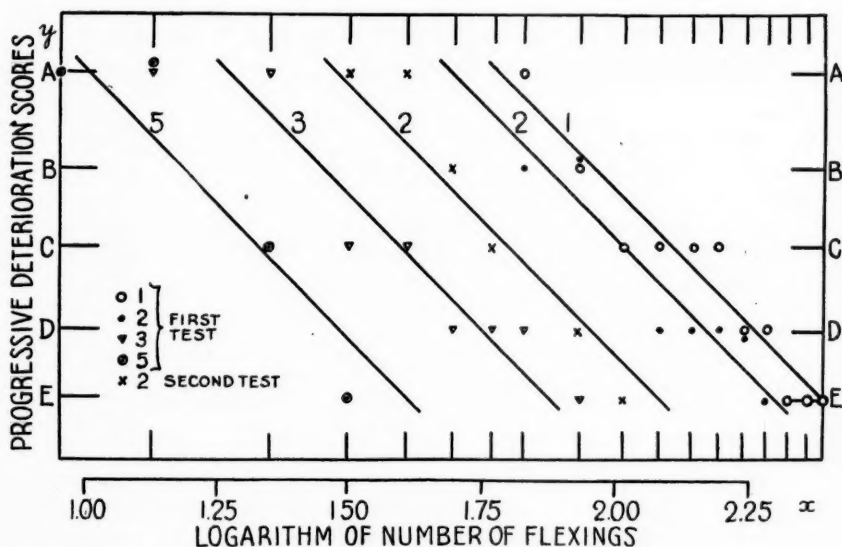
[illegible]

FIG. 1.—Regressions of scores on logarithmic flexings.

ure 1). We notice that these considerations lead only to a determination of the relative scores for A-E; we may afterward change them, either by adding a constant to all, or by multiplying them by a constant.

3.2. STATISTICAL DETERMINATION OF THE SCORES

In the mathematical treatment we denote the quantitative scores in general by y and, in particular, by the same letters as were used for the qualitative grading.

Then the total variation of the scores is measured by the total sum of squares of deviations of the scores y from the general mean, i.e.:

$$S(y - \bar{y})^2$$

Since y takes one of the five yet undetermined values A, . . . E, this sum of squares is a homogeneous quadratic expression in A, . . . E. The expression may conveniently be represented by the symmetrical matrix of coefficients:

$$\{T\} = \begin{pmatrix} t_{AA} & t_{AB} & t_{AC} & t_{AD} & t_{AE} \\ & t_{BB} & t_{BC} & t_{BD} & t_{BE} \\ & & t_{CC} & t_{CD} & t_{CE} \\ & & & t_{DD} & t_{DE} \\ & & & & t_{EE} \end{pmatrix}$$

where t_{AA} is the coefficient of A^2 and t_{AB} that of $2AB$. The obvious big differences between the same rubber on two occasions leads us to treat all 18 tests as though they had different means, so that the total sum of squares may be partitioned into the sum of the squares between tests and the sum of the squares within tests. The same analysis is made on the products of y and x ($=\log$ flexings,) and on squares of x . The former is in terms of linear functions of A, . . . E, conveniently represented by the coefficients in order; while the latter is, of course, the usual analysis of variance expressed by simple numbers.

The process is made clear by the actual arithmetic rather than by mathematical formulas.

The sum of squares within tests is:

$$Sy^2 - \Sigma(Y_r \bar{y}_r)$$

where S denotes summation over the whole data, $Y_r \bar{y}_r$ are the subtotal and mean for the r th test, and Σ denotes summation over the different tests.

Remembering that y takes one of the five undetermined values A, . . . E, we see that in terms of the matrix of coefficients:

$$Sy^2 = \begin{pmatrix} 18 & & & & \\ & 23 & & & \\ & & 22 & & \\ & & & 22 & \\ & & & & 19 \end{pmatrix}$$

The terms in the $\Sigma(Y_r \bar{y}_r)$ are found from the bottom marginal subtotals in Table 2. For example, the coefficient of $2BC$ is:

$$\frac{1 \times 4}{11} + \frac{2 \times 1}{8} + \frac{0}{8} + \dots + \frac{1 \times 1}{7} = 3.330$$

Hence:

$$\Sigma(Y_r \bar{y}_r) = \begin{pmatrix} 5.345 & 2.328 & 3.570 & 3.647 & 3.110 \\ & 10.637 & 3.330 & 3.637 & 3.069 \\ & & 6.686 & 4.181 & 4.232 \\ & & & 6.566 & 3.970 \\ & & & & 4.620 \end{pmatrix}$$

The sum of squares within tests which we denote by W_{yy} is, therefore:

$$W_{yy} = \begin{Bmatrix} 12.655 & -2.328 & -3.570 & -3.647 & -3.110 \\ & 12.363 & -3.330 & -3.637 & -3.069 \\ & & 15.314 & -4.181 & -4.232 \\ & & & 15.434 & -3.970 \\ & & & & 14.380 \end{Bmatrix} \dots (3.21)$$

We may note, as a check, that all rows of this matrix (completed symmetrically across the diagonal) add to zero.

We now find the sum of products of y and x within tests:

$$= S(yx) - \Sigma(Y_r \bar{x}_r)$$

where S and Σ have the same meanings as before.

$S(yx)$ is a linear function in $A, \dots E$, the coefficients being found by summing the products of x and the right hand marginal subtotals in Table 2. The coefficient of A , for example, is:

$$2 \times 0.954 + 4 \times 1.130 + \dots + 1 \times 1.932 = 25.477$$

The total sum of products is, therefore:

$$S(yx) = 25.477 \quad 40.930 \quad 39.590 \quad 41.732 \quad 37.867$$

The subtotals and means of x for the different tests are given in Table III, so that we sum the products of entries in a bottom margin of Table II, and the corresponding \bar{x} from Table III, to give $\Sigma(Y_r \bar{x}_r)$.

For example, the coefficient of A is:

$$1 \times 2.1648 + 2 \times 1.6013 + \dots + 1 \times 1.6686 = 29.717$$

Hence:

$$\Sigma(Y_r \bar{x}_r) = 29.717 \quad 42.934 \quad 39.740 \quad 39.307 \quad 33.899$$

By subtraction we find the within sum of products:

$$W_{xy} = -4.240 \quad -2.004 \quad -0.150 \quad 2.425 \quad 3.968 \quad \dots (3.22)$$

As a check we notice that the sum of the coefficients is zero.

Finally we evaluate the within sum of squares for x . $S(x^2)$ is given by the sum of products of the numbers in the extreme right-hand margin of Table II and the squares of the corresponding x .

$$S(x^2) = 342.428$$

$\Sigma(X_r \bar{x}_r)$ is the sum of products of subtotals and means in Table III.

$$\begin{aligned} \Sigma(X_r \bar{x}_r) &= 23.813 \times 2.1648 + \dots + 11.680 \times 1.6686 \\ &= 339.254 \end{aligned}$$

Hence the within tests sum of squares is:

$$W_{xx} = 3.174 \quad \dots (3.23)$$

3.3. MINIMIZING THE ERROR

Following a procedure known as the Analysis of Covariance explained in "Statistical Methods for Research Workers," and forgetting for the moment that

TABLE III
SUMS AND MEANS OF $x = \text{LOG FLEXINGS}$

Rubber number	1	2	3	4	5	6	7	9	10	Grand totals and general mean
First test $\dots \left\{ \begin{array}{l} n \\ X = \frac{\Sigma x}{x} \end{array} \right.$	11 23.813 2.1648	8 16.733 2.0916	8 12.810 1.6013	3 3.436 1.1453	4 4.934 1.2335	4 7.860 1.9650	4 6.152 1.5380	6 12.617 2.1028	7 13.969 1.9956	7 104 185.596 1.78458
Second test $\dots \left\{ \begin{array}{l} n \\ X = \frac{\Sigma x}{x} \end{array} \right.$	11 21.013 1.9103	7 12.343 1.7633	7 11.680 1.6686	4 6.152 1.5380	1 1.130 1.1300	5 8.396 1.6792	4 5.587 1.3963	3 5.291 1.7637	7 11.680 1.6686	

TABLE IV
SUBTOTALS AND MEANS OF $w = x + y$

Rubber number	1	2	3	4	5	6	7	9	10	Totals
First test $\dots \dots \dots \left\{ \begin{array}{l} n \\ \frac{\Sigma w}{w} \end{array} \right.$	11 23.130 2.1027	8 16.123 2.0154	8 12.717 1.5896	3 3.935 1.3117	4 5.306 1.3265	4 7.896 1.9740	4 5.861 1.4652	6 12.945 2.1575	7 14.845 2.1207	55 102.758 1.86833
Second test $\dots \dots \dots \left\{ \begin{array}{l} n \\ \frac{\Sigma w}{w} \end{array} \right.$	11 21.094 1.9176	7 12.551 1.7930	7 11.561 1.6516	4 5.861 1.4653	1 1.276 1.276	5 8.578 1.7156	4 5.477 1.3692	3 5.764 1.9213	7 11.152 1.5931	49 83.314 1.70029
Both tests $\dots \dots \dots \left\{ \begin{array}{l} n \\ \frac{\Sigma w}{w} \end{array} \right.$	22 44.224 2.0102	15 28.674 1.9116	15 24.278 1.6185	7 9.796 1.3994	5 6.582 1.3164	9 16.474 1.8304	8 11.338 1.4172	9 18.709 2.0788	14 25.997 1.8659	104 186.072 1.78915

W_{yy} and W_{xy} are functions of A, . . . E, we find the common coefficient of regression b , of y on x for all tests:

$$b = W_{xy}/W_{xx}$$

The portion of the within sum of squares of y accounted for by regression is:

$$(W_{xy})^2/W_{xx}$$

We may in fact analyze the within variance in the conventional way:

	Degrees of freedom	Sum of squares
Regression of y on x	1	$(W_{xy})^2/(W_{xx})$
Deviations from the regression lines.....	85	$W_{yy} - (W_{xy})^2/(W_{xx})$
Within tests	86	W_{yy}

The metrical values for A, . . . E have, however, yet to be assigned, and it is clear that the proper values are those which minimize error, *i.e.*, sum of squares of deviations from the regression lines, and maximize the portion accounted for by regression. This is achieved by maximizing the ratio of regression square to total sum of squares, *i.e.*:

$$(W_{xy})^2/W_{xx}W_{yy}$$

for variations in A, . . . E.

Differentiating in turn with respect to A, . . . E, we find a set of five linear simultaneous equations in A, . . . E, of which the coefficients and right-hand sides may be written as:

$$W_{yy} = k W_{xy}$$

where $k = W_{xy}/W_{xx}$ when the solution values for A, . . . E are inserted. Since k is the same as all equations, and since the scores are in any case multiplicable by any constant, we may drop the k and solve the equations:

$$W_{yy} = W_{xy}$$

Moreover, since any constant may be added to all the scores, we may set, *e.g.*, $E=0$, and solve the four equations formed from the above by dropping the last equation and the last term of each of the remaining four.

3.4. ARITHMETICAL PROCEDURE

As before, the actual arithmetic calculations will make the method clear. The four equations in A,B,C,D are:

A	B	C	D
12.655	- 2.328	- 3.570	- 3.647 = 4.240
- 2.328	12.363	- 3.330	- 3.367 = 2.004
- 3.570	- 3.330	15.314	- 4.181 = 0.150
- 3.647	- 3.637	- 4.181	15.434 = - 2.425

Solution proceeds in the usual way by reducing the number of equations by one at each stage, and we finally find:

$$\begin{aligned} A &= 0.4927 \\ B &= 0.3465 \\ C &= 0.2280 \\ D &= 0.1027 \\ E &= 0 \end{aligned} \quad \dots (3.41)$$

The regression coefficient is found from W_{xy}/W_{xx} where now, of course, we may substitute the above scores in the expression for W_{xy}

$$b = -0.8093 \quad \dots (3.42)$$

For reasons which will appear shortly, we choose to scale the scores so that the regression coefficient is -1 . We therefore divide the above scores by 0.8093 . Further, we subtract the value for C from all scores so as to make C zero, thus arriving at the scores in the second column:

		Final scores	
A	0.6088	0.327	
B	0.4282	0.146	
C	0.2818	0	
D	0.1269	-0.155	
E	0	-0.282	... (3.43)

4. DETERMINATION OF MEAN STRENGTHS

We are now able to calculate a mean for each test which fairly represents the strength of the rubber under test.

Since we have arranged the regression coefficient to be -1 , the regression line which best fits the data for one test is:

$$y = \bar{y} - (x - \bar{x})$$

This line intersects the axis $y=0$ at:

$$x_0 = \bar{x} + \bar{y} = \bar{x} + \bar{y} = \bar{w}$$

Hence we may find x_0 by writing down for each observation from the first A to the last E the sum w of the x and the score y , and averaging. Thus for No. 2 in the first test we have:

	x	y	$W = x + y$
A	1.829	0.146	1.975
B	1.932	0.146	2.078
C	2.015	0.000	2.015
D	2.084	-0.155	1.929
D	2.145	-0.155	1.990
D	2.197	-0.155	2.042
D	2.244	-0.155	2.089
E	2.287	-0.282	2.005
$\bar{8}$			$\Sigma w = 16.123$
			$w = 2.0154$

Alternatively, since Σx is already known from Table III we may find thus:

$$\begin{aligned} \Sigma w &= \Sigma x + \Sigma y \\ &= 16.733 + 2(0.146) - 4(0.155) - (0.282) \\ &= 16.123 \\ \therefore \bar{w} &= 2.0154 \end{aligned}$$

The mean strength of the 18 pieces are listed in Table IV.

We may interpret \bar{w} as the estimate of the log of the number of flexings required to reduce the sample to condition, C, i.e.:

$$\text{antilog } 2.0154 = 103.6$$

Hence 103,600 flexings reduce the sample to condition C. However, we wish to emphasize that nothing is gained by converting back to actual flexings, since standard errors will be found for, and comparisons will always be made between, the \bar{w} for different rubbers. Hence it is more convenient to regard \bar{w} as the real measure of rubber flexing resistance.

We may notice also that there is no particular reason for having made $C=0$. If all the scores are increased by a constant, the values of \bar{w} are all increased by the same constant, and consequently comparisons will be unaltered.

5. THE ANALYSIS OF VARIANCE

We may now proceed to make an Analysis of Variance on the quantities $w=x+y$. In the normal way the various items in the analysis would be obtained from the corresponding entries in the Analysis of Variance and Covariance of x and y . In the present case, however, we find it more convenient to proceed from Table IV, showing the subtotals and means for the 18 tests for the nine types of rubber, and for the first and second replication. From this table we calculate the sums of squares for the 17 degrees of freedom between tests, analyzed into:

	Degrees of freedom
Between rubbers	8
Between replications	1
Interaction	8
Between tests	17

Thus, for example, the sum of squares between tests is found by summing for all tests the product of the subtotal and mean and subtracting the product of grand total and general mean:

$$= 23.130 \times 2.1027 + \dots + 11.152 \times 1.5931 - 186.072 \times 1.78915$$

Similarly the sum of squares for differences between rubbers is found from the subtotals and means for the two replications combined

$$= 44.224 \times 2.0102 + \dots + 25.997 \times 1.8659 - 186.072 \times 1.78915$$

The within sum of squares for y is found from the within matrix (3.21) by multiplying the entries of each row by the scores (3.43) giving the subtotals in the right-hand margin; and then again multiplying these subtotals by the scores and summing. Omitting the middle row column (since $C=0$) we find:

$$\left\{ \begin{array}{cccc} 12.655 & -2.328 & -3.647 & -3.110 \\ & 12.363 & -3.637 & -3.069 \\ & & 15.434 & -3.970 \\ & & & 14.380 \end{array} \right\} \begin{array}{l} 5.2406 \\ 2.4729 \\ -2.9963 \\ -4.9048 \\ \hline 3.9223 \end{array}$$

The portion of this within sum of squares which is accounted for by regression is:

$$b^2 W_{xx} = W_{xx}$$

since b has been made $= -1$

From (3.23) we have:

$$W_{xx}=3.174$$

Hence the sum of squares for deviations from the regression line, *i.e.*, the within sum of squares for *w* is:

$$3.922-3.174=0.748$$

The only question which remains before assembling the various items of the Analysis of Variance is the allocation of degrees of freedom. There are in all $103-17=86$ degrees of freedom for within sum of squares of *w*. Of these the fitting of the regression would normally remove one degree of freedom. Since, however, the five values for A, . . . E have also been ascertained (representing three independent parameters), we have the following partition of degrees of freedom:

Regression and allocation of scores.....	4
Error = deviations from regression lines.....	82
Within tests	86

We may therefore assemble the Analysis of Variance in Table V.

TABLE V
ANALYSIS OF VARIANCE OF *w*

	Degrees of freedom	Sum of squares	Mean square
Between kinds of rubber.....	8	5.857	0.732
Within kinds of rubber			
Between replications	1	0.733	0.733
Interaction	8	0.949	0.118
Between tests	17	7.539	
Error = within tests	82	0.748	0.00912
Total	99	8.287	

6. DISCUSSION OF THE ANALYSIS OF VARIANCE

The first thing which may be noted about Table V is how surprisingly successful the fitting of a set of regressions of common slope has been in absorbing the variance. Out of 99 degrees of freedom, the 82 degrees of freedom for error account for only about 11 per cent of the total variance.

If we assume that the only source of error were that due to the discontinuity of the qualitative scale, then the mean square for error should be of the order of $h^2/3$, where $2h$ is the distance between successive points on the scale. Putting approximately:

$$\begin{aligned} 8h &= 0.327 - (-0.282) \\ &= 0.609 \\ h &= 0.076 \\ h^2/3 &= 0.0019 \end{aligned}$$

Thus the calculated standard error is a little over twice the absolute theoretical minimum.

Some improvement may still be possible in the accuracy of qualitative scoring, but this source of error is negligible compared with a very grave source of error which will appear immediately.

The numbers \bar{w} in Table IV can be regarded as true measures of the flexing resistances of the piece of rubber in each of the 18 particular tests. They are, however, in no sense measures of the flexing resistance of that kind of rubber, unless the same rubber gives consistent results in a repeated test. If the only source of error were errors of observation, then the mean square for replication, and for interaction between rubbers and replication, would both be comparable with the mean square for error. Actually both are so very much greater that there is no shadow of doubt about their significance.

Of course it may be that the additional variability is due to the inherent non-uniformity of each kind of rubber, and as such is unavoidable. There is, however, further evidence that this is not the complete explanation, for we may compare the mean square for replication against the mean square for interaction, giving a variance ratio of 6:2, which is above the 5 per cent level of significance. Thus it appears that, even granting non-uniformity of the material, the average strength was significantly lower on the second series of tests than on the first.

We therefore suggest that the testing cannot be said, in the present case, to be proceeding satisfactorily. It should be possible to bring the mean square within rubbers (*i.e.*, nine degrees of freedom, replication + interaction), down to a figure comparable with error.

If, however, this proves to be impossible, then the observed variance for within rubbers is the appropriate one to use for testing the significance of comparisons between rubbers.

7. COMPARISON OF TEST MEANS

If we denote the error or mean square by $\sigma^2=0.00912$, then the variance of any \bar{w} based on n observations is σ^2/n . For example, for rubber No. 1 in test 1 we have:

$$\begin{aligned}w &= 2.1027 \\n &= 11 \\ \text{variance} &= 0.00083 \\ \text{standard error} &= 0.0288\end{aligned}$$

whereas for the second test on the same rubber:

$$\begin{aligned}\bar{w} &= 1.9176 \\n &= 11 \\ \text{variance} &= 0.00083\end{aligned}$$

The standard error of the difference is, therefore:

$$\sqrt{2 \times 0.00083} = 0.0407$$

the difference of the means is:

$$2.1027 - 1.9176 = 0.0851$$

and is therefore just significant (5 per cent).

It should be remarked, however, that these tests of significance and those made in the Analysis of Variance are slightly vitiated by the errors of the determination of the quantitative scores A, . . . E. Since, however, the exact tests are

elaborate, and since, moreover, the scores will have to be redetermined on more extensive data, we may content ourselves at this stage with approximate tests.

8. THE ADEQUACY OF THE LOGARITHMIC SCALE

It remains to be considered whether there still are differences between the rubbers, other than those expressed by the mean \bar{w} . In other words, has the logarithmic scaling of the number of flexings been successful? The smallness of the residual variance, already pointed out, shows that, if there are any other differences between tests, they must be very slight.

Owing to scantiness of the data, particularly at the lower end of the log scale, and the failure to obtain true replication, it is hardly worth while to make a thorough test of the adequacy of the log scale, but we may at least indicate how this should be done, and leave the more thorough examination to a later date.

Differences between tests, if they exist, will be revealed mainly in heterogeneity of the regressions of the quantitative scores y on x . We have arranged for the

TABLE VI
RESIDUAL REGRESSIONS OF SCORES IN LOG FLEXINGS

First test rubber number	\bar{w}	δb	$S(x-\bar{x})^2$	$(\delta b)^2 S(x-\bar{x})^2$
1.....	2.1027	-0.003	0.339	0.0000
2.....	2.0154	+0.086	0.179	0.0013
3.....	1.5896	+0.091	0.494	0.0041
5.....	1.3260	-0.156	0.173	0.0042

common regression to be -1, but we may calculate the individual regressions of y on x in each test. For example, in rubber No. 2 first test we find:

$$\begin{aligned} S(y-\bar{y})(x-\bar{x}) &= -0.1638 \\ S(x-\bar{x})^2 &= 0.1757 \\ b &= -0.9323 \end{aligned}$$

This individual regression differs from the general regression, which was made equal to -1, by an amount:

$$\delta b = +0.0677$$

The difference is, however, not significant, for if we take:

$$(\delta b)^2 \times S(x-\bar{x})^2 = 0.00081$$

we find a mean square less than the mean square for error. The differences of individual regressions from the general regression for four typical tests are listed in Table 6, which suggests that there are no differences in the rates of breakdown when expressed on a logarithmic scale.

If it appeared that the residual regressions were heterogeneous, there would be still the question of whether the heterogeneity could be removed by a slight alteration in scaling. Such a complication would be very unwelcome, but a glance at the four tests in Table 6 shows that it is unlikely that this would be necessary. The need of a different scaling would be indicated by a tendency for test-pieces with a high mean to break down too slowly, and those with a low mean to break down too quickly, or *vice versa*. But it appears that, of the four listed, the test with the highest mean has a very slight negative regression; the next highest, positive; the second lowest, positive; and the lowest, again negative.

The success of the log scale is again brought out in Figure 1, which shows y plotted against x for five of the tests, together with the five regression lines of slope -1 , which best fit the five sets of data.

Finally, although it is very probable that more extensive data would show no differences whatever between rubbers other than those indicated by their mean \bar{w} , we must point out that, even if slight residual differences remain, these will be of no practical consequence, and the methods of the analysis above will be quite adequate for all practical purposes.

9. NON-MATHEMATICAL SUMMARY

Various kinds of rubber are subjected to flexing by a machine. At intervals the machine is stopped, and the numbers of flexings are noted, and the qualitative state of breakdown of the rubber also is noted by comparison with a scale of samples, lettered A, B, . . . E.

The analysis of the present paper shows that the intensity of treatment to which a test-piece has been subjected should be measured by x , the logarithm of the number of flexings. It is then a straightforward matter to calculate the quantitative scores y , which should be assigned to the qualitative scale.

When this has been done, it is shown that the rates of breakdown, measured against a log scale, are the same for all test-pieces, and the behavior of a test-piece may therefore be completely summarized in a single number:

$$\bar{w} = \bar{x} + \bar{y}$$

i.e., the mean of the x 's plus the mean of the scores from the first A to the last E.

The mean \bar{w} is, therefore, the true measure of the flexing resistance of the rubber. A high precision will be obtainable by this method, though it appears in the present data that there are big differences in repeated tests on the same kind of rubber.

It is hoped that a more extensive body of data will soon be available for a more thorough investigation on the same lines. In the experiment on which it is based, it would be desirable to use a rather more finely graduated qualitative scale, and to take observations at intervals which are equally (or approximately equally) spaced on a logarithmic scale.

ACKNOWLEDGMENTS

I am indebted to the Research Association of British Rubber Manufacturers, who suggested the problem and supplied the data, and to R. G. Newton for criticism of the typescript. The data used to illustrate the statistical methods were kindly placed at the disposal of the author by Dr. Newton, who was also the source of information on matters of laboratory technique.

REFERENCES

- The subject of discriminant function analysis and qualitative scoring is very recent and incomplete. An example resembling the method of the present paper will however be found in Ex. 46.2, Chapter VIII, of the seventh edition of R. A. Fisher, "Statistical Methods for Research Workers", Oliver & Boyd, Edinburgh.
- The theory of the Test of Significance is given in R. A. Fisher, "The Sampling Distribution of Some Statistics Obtained from Non-Linear Equations", *Annals of Eugenics*, Vol. 9, pp. 238-249.
- Further information on the testing technique and references to other work will be found in R. G. Newton. "A Qualitative Method of Expressing Flex-Cracking Results", *Trans. Inst. Rubber Ind.*, Vol. 15, pp. 172-184.

MACHINE AND METHODS FOR TESTING MECHANICAL STABILITY OF LATEX *

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The mechanical stability of a sample is one of the important factors in processing latex. Therefore it is necessary to have a testing method which is simple and reasonably rapid, yet gives accurate and reproducible results.

The various methods of testing mechanical stability where latex is used and tested result in a different standard at each place and create confusion when it is necessary to compare results obtained by different procedures.

This paper gives the results obtained with the original standard test and modifications which were introduced in an attempt to establish a universal and more accurate test for determining the mechanical stability. In this work three different methods were used, and in each one two different types of stirrers were tried (Figures 1 and 2).

One machine, used as a high-speed stirrer, was a Benedict Indestructo mixer, No. 53, Serial No. 23270, 105 to 120 volts, 70 watts, and 25 to 60 cycles. The other machine was a constant-speed stirrer built at the Firestone Laboratories. It consists of a vertically mounted Bodine synchronous motor of 1800 r. p. m., 110 volts, 7.4 amperes, 0.2 horsepower, and 60 cycles, with a 20.15-cm. (8.06-inch) wooden pulley mounted on the motor shaft, and a rubber fiber belt connecting the pulley to a stainless steel shaft 2.5 cm. (1 inch) in diameter, mounted vertically in a steel tripod. The steel shaft is furnished with a metal propeller attached to the lower end, and this makes up the stirring element. The motor support and steel tripod are mounted permanently on a wooden base plate. This construction is not to be considered the best equipment that could be built, but it did serve its purpose for this work. Plans are being drawn up for a simpler and more permanent piece of apparatus.

METHODS USED

Method 1A is carried out on the Benedict mixer. A 50-cc. sample of the latex is obtained from the drum and is stirred at 25° C in a 118-cc. (4-ounce) square bottle, with a high-speed stirrer, until completely coagulated. The stirrer is equipped with a hexagonal, slotted propeller, as shown in Figure 3.

Method 1B is exactly the same as 1A, except that the test is carried out on the constant-speed stirrer, which is also equipped with the hexagonal slotted propeller.

Method 2A is a modification wherein an 80-cc. sample of latex with 50 per cent total solids and 0.5 per cent ammonia is held at 35° C, and is stirred in a 250-cc. round bottle with the Benedict mixer.

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Method 2B is the same as 2A, except that the constant-speed stirrer is used.

Method 3A is a slight modification of Method 1A, using a sample diluted with distilled water to a total solids content of 50 per cent and 0.5 per cent ammonia. The Benedict mixer is used in this case.

Method 3B is the same as 3A, except that the constant-speed stirrer is employed.

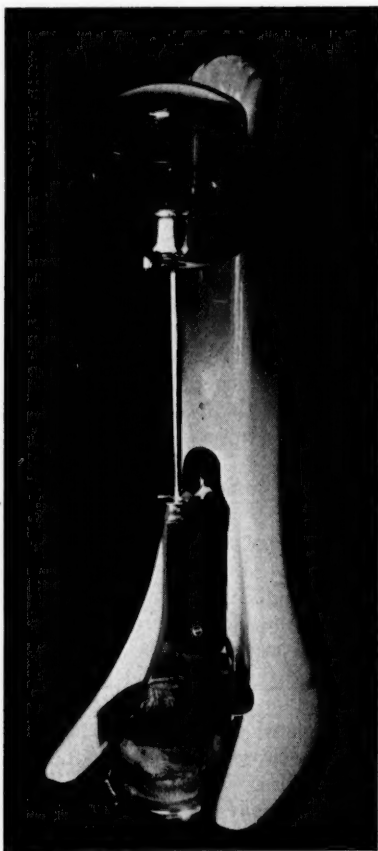


FIG. 1.—Benedict stirrer.

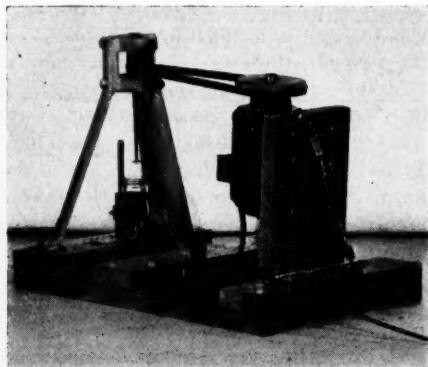


FIG. 2.—Constant-speed stirrer.



FIG. 3.—Propeller.

SPEED MEASUREMENTS

The shaft speed in r. p. m. of each stirrer was measured by an Edgerton stroboscope under various operating conditions. This stroboscope was capable of measuring speeds directly, as shown on the scale, up to 3000 r. p. m. Beyond this point, factors had to be used, when perfect synchronization was obtained, to calculate the shaft speed.

The constant-speed stirrer was operated in media of different viscosities. When running free, the stirring element of this machine ran at 13,420 r. p. m. On checking the same shaft in such media as water, concentrated latex, glycerol,

and Karo sirup that had been cooled to 10° C to make a very viscous medium, this speed remained constant over 15-minute periods. In view of these results, there is no question as to the constant speed of this stirrer during any test.

The new Benedict mixer was tested with various latex samples of high total solids content for constancy of speed by means of the stroboscope. This machine was strongly affected by the loads under which it was running. Under load of a sample of latex of 60 per cent total solids, the speed varied from 17,000 to 20,000 r. p. m. during the actual test; after coagulation took place, the speed was reduced to a much lower value. In samples of total solids contents of 40 and 50 per cent, the speed variations were not very great. Although there was considerable variation in the speed of the Benedict mixer under load, the variation over actual testing periods tended to average itself, and in some cases the speed was very close to 19,000 r. p. m. during the test. In the samples of latex having 40 and 50 per cent solids, the average was very good under what might be termed normal operating conditions. However, in many cases conditions were not normal, and in these cases the speed of the machine varied considerably and gave different results.

The results above indicate that the constant-speed stirrer is very reliable, and that results on the Benedict mixer averaged fairly well over a run, but in many tests the results were changed by the inability of the mixer to keep a constant r. p. m. This was due to change in operating conditions, which must be expected when handling such materials as latex, where coagulum is introduced during the test. If the coagulum comes into contact with the shaft in any way to create high friction and thereby a braking action, it upsets the value for this particular test.

EXPERIMENTAL DATA

Ten samples of latices, selected over a period of one year to give as wide a range as possible, were taken for these tests. Each sample was run at least twice according to the methods described above, and the data obtained are given in Table I. The constant-speed stirrer gives the most accurate results in all cases. In this present setup, the constant-speed stirrer requires a longer time for end-points in the test. Methods 1A and 1B give extremely rapid results and, because of this, it is impossible to bring out small differences in stability between two samples. Methods 2A and 2B correct this somewhat, but still do not give the desired differentiation between samples. If, however, we consider methods 3A and 3B, there are larger differences between samples.

The results presented in Figure 4 and Table I in many cases hardly seem to show the necessity for using a constant-speed stirrer. However, in some cases it was necessary to run a third sample when using a Benedict stirrer because the original results were too far apart to average.

The following data are very convincing as to the need of a constant-speed stirrer in the latex industry. The Firestone Tire & Rubber Company has need for determining the mechanical stabilities of latices at four widely separated points. Even though the specifications for test were drawn up at the home office and equipment was purchased in each case from the same company under specifications, and checked at the home laboratories with the determination of factors if necessary, there was a good deal of confusion and inconsistency in the results obtained at the various places. These discrepancies brought about the work which is presented in this paper. The following results indicate difficulties which are very apt to be encountered with the use of the malted milk (Benedict) type of mixer.

The test results (Table II) were first obtained at the home laboratories with samples selected and prepared at that point. These results were not furnished to the subsidiary plants, but they in turn determined the stabilities, on both the Benedict mixer and the constant-speed instrument, of the samples which had been prepared at the home plant. Table II shows the wide discrepancies which can be encountered with what might seem at first to be a very reliable and accurate method of determining mechanical stabilities, but with which it seems practically impossible to duplicate results in different laboratories. Here the constant-speed stirrer has shown its reliability.

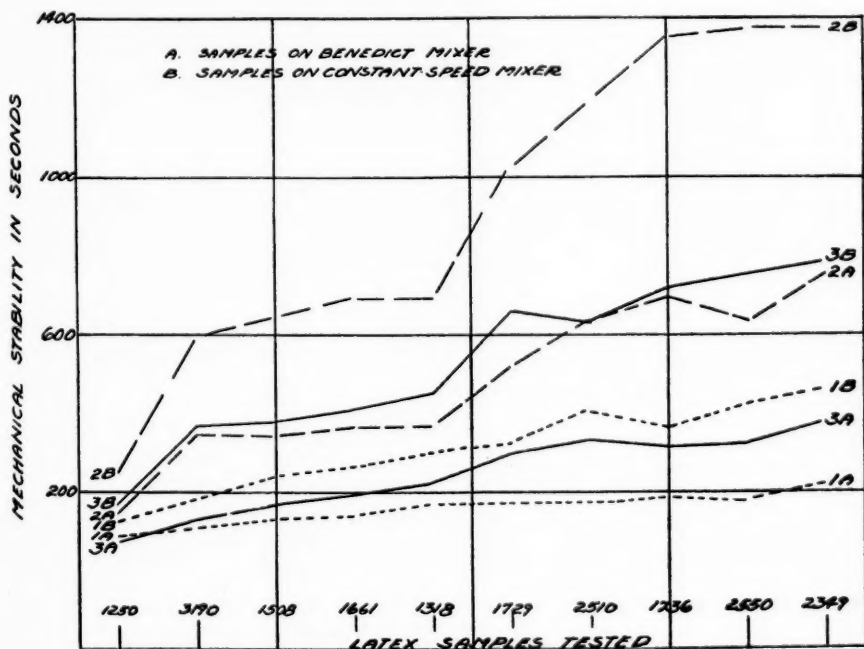


FIG. 4.

There probably will be need for further standardization of this test, but it can readily be seen that it merits adoption.

Tachometers or other speed-determining instruments may be attached to the Benedict mixer. In this way a record may be kept of the speed from time to time, an average may be made over a period of time, and a factor may be introduced for correcting the result in seconds. But the observation of the end-point in any mechanical stability test requires the attention of the operator at all times. Also, any instrument which must be attached to the malted milk mixer for recording speed, etc., immediately removes its only advantage over the constant-speed mixer: cheapness. The cost of the constant-speed stirrer is slightly higher, but will be less than that of a Benedict mixer with all other instruments attached. The constant-speed stirrer is much simpler to operate and the test in itself is simpler, inasmuch as the operator has only the sample under test to consider.

TABLE I
 DUPLICABILITY OF RESULTS IN DETERMINING MECHANICAL STABILITIES

Drum No.	Total solids (%)	Method 1A			Method 1B		
		Run 1	Run 2	Av.	Run 1	Run 2	Av.
1250.....	61.25	92	102	97	130	128	129
1318.....	60.91	175	166	171	306	295	301
1508.....	60.92	130	143	137	249	233	241
1661.....	60.82	128	155	142	253	274	264
1729.....	59.78	176	170	173	317	326	322
1736.....	61.42	180	186	183	357	360	359
2349.....	61.87	208	215	212	436	463	450
2510.....	62.86	170	159	165	425	390	408
2550.....	62.81	180	161	171	423	419	421
3190.....	60.72	110	114	112	217	165	191

Drum No.	Total solids (%)	Method 2A			Method 2B		
		Run 1	Run 2	Av.	Run 1	Run 2	Av.
1250.....	—	151	135	143	260	251	256
1318.....	—	355	374	365	698	694	696
1508.....	—	352	337	345	646	640	643
1661.....	—	369	374	372	701	695	698
1729.....	—	529	522	526	1021	1017	1019
1736.....	—	710	687	699	1350	1339	1345
2349.....	—	728	760	744	1380	1352	1366
2510.....	—	627	645	636	1160	1176	1168
2550.....	—	625	639	632	1380	1358	1369
3190.....	—	343	355	349	585	583	584

Drum No.	Total solids (%)	Method 3A			Method 3B		
		Run 1	Run 2	Av.	Run 1	Run 2	Av.
1250.....	—	73	72	73	163	167	165
1318.....	—	249	210	230	457	442	450
1508.....	—	163	170	167	389	375	382
1661.....	—	185	196	191	413	401	407
1729.....	—	297	300	299	660	672	666
1736.....	—	313	300	307	704	713	709
2349.....	—	375	361	368	770	782	776
2510.....	—	331	326	329	632	626	629
2550.....	—	333	309	321	755	738	747
3190.....	—	129	123	126	393	343	368

TABLE II
 MECHANICAL STABILITY TESTS ON LATEX

Sample	Methods 2B and 2A					
	Constant-speed mixer			Benedict mixer		
	Plant 1	Plant 2	Plant 3	Plant 1	Plant 2	Plant 3
1250.....	160	160	150	165	145	120
1661.....	520	530	530	540	475	240
1729.....	450	435	480	440	355	240
2349.....	480	480	460	550	440	255
3190.....	315	325	375	325	280	140

A point which has not been studied in any detail in this investigation has been the type of propeller used on the stirring element. This should be given some consideration, as the propeller itself can affect the result if it is not readily self-cleaning when pieces of coagulum are picked up on the edges which cause the major portion of the agitation. A propeller should be adopted which can be easily reproduced in any machine shop and not have to be stamped out with a die.

The type of container, the quantity of latex, specifications as to solids content, and ammonia content are all very important in this test. However, the two factors of solids content and ammonia content need not be introduced into a standard specification if the equipment itself is standardized sufficiently to give reproducible results at different laboratories. If such specifications are followed, an ammonia content can be decided by the laboratories using this type of test.

SUMMARY

Methods and machines have been studied for making mechanical stability tests on latices. The results indicate that a constant-speed machine will give reproducible results at widely separated laboratories when test samples of fixed solids content are used.

ACKNOWLEDGMENT

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CONTROL OF GELLING IN VULCANIZING CEMENTS

NITROPARAFFINS AND CHLORONITROPARAFFINS AS INHIBITORS *

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The broad application of ultraaccelerators to vulcanizing rubber cements has been handicapped by the formation of irreversible gels, presumably due to partial or complete vulcanization while in solution. The gelling tendency can be overcome by the use of so-called two-part cements, as illustrated in recipe I. Rubber, zinc oxide, and sulfur are mixed on the usual type of mill and then dissolved in a suitable solvent to form one part; rubber and accelerator or accelerators, with or without zinc oxide, and similarly mill-mixed, are dissolved in the same solvent to form the second part. Mixing these two parts in the proper proportions produces a cement containing all the necessary ingredients in the proper proportions for vulcanization. With ultraaccelerators, the mixed cement gels or vulcanizes within a period of hours or days, depending on the accelerator and the accelerator-sulfur ratio. The gel constitutes an economic loss. While two-part cements overcome this gelling, they are not economical of labor and space.

It has been found that nitroparaffins¹ and their derivatives will inhibit gelling of vulcanizing cements for long periods. Thus, with many accelerator-sulfur combinations it is possible to make direct mill mixes, followed immediately by churning in the solvent containing the antigel agent. This eliminates half of the mixing and churning usually necessary with ultraaccelerated cements, and permits any unused cement to be stored for use later.

NITRO- AND CHLORONITROPARAFFINS AS RUBBER SOLVENTS

Tests with masticated pale crepe indicate that nitroparaffins are not solvents for rubber in the usual sense, whereas certain chlorosubstituted nitroparaffins are good solvents. The solvent power of the latter varies with the structure of the compound. In the tests outlined in Table I the following two-part cement was used, made up to 10 per cent rubber content, with benzene as the solvent:

RECIPE I

	A	B
Pale crepe rubber.....	100.0	100.0
Zinc oxide	0.5	0.5
Sulfur	2.5	—
Zinc dibutyldithiocarbamate	—	1.0
	103.0	101.5

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 33, No. 6, pages 809-812, June 6, 1941. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its 97th meeting at Baltimore, Maryland, April 5, 1939. The use of nitroparaffins and their derivatives as antigel agents for rubber cements is covered by patent applications assigned to the Commercial Solvents Corporation.

To the indicated quantity of mixed cement (Table I) small amounts of the compound to be tested were added, followed by vigorous shaking. This was continued until a precipitate of rubber appeared that would not redisperse on shaking, or until it was evident that no precipitation would occur.

TABLE I

EFFECT OF NITRO- AND CHLORONITROPARAFFINS ON SOLUBILITY OF RUBBER
IN A 10 PER CENT RUBBER-IN-BENZENE CEMENT

Volume of cement (cc.)	Organic compound	Volume used (cc.)	Result
20	Nitromethane	7	Pptn.
20	Nitroethane	14	Pptn.
20	1-Nitropropane	26	Pptn.
20	2-Nitropropane	22	Pptn.
20	1-Nitro- <i>n</i> -butane	64	Pptn.
20	2-Nitro- <i>n</i> -butane	61	Pptn.
20	1-Nitro-2-methylpropane	54	Pptn.
20	2-Nitro-2-methylpropane	39	Pptn.
10	1-Chloro-1-nitropropane	50	No pptn. ^a
10	1,1-Dichloro-1-nitropropane	50	No pptn. ^a
10	2-Chloro-2-nitropropane	50	No pptn. ^a

^a These were at all times smooth homogeneous cements.

TABLE II

NITRO- AND CHLORONITROPARAFFINS IN AN ACCELERATED TEST AT
50° C IN BENZENE^a

Antigel	Vol. ^b used (cc.)	Hours to gel
Blank	0	4.5
Nitromethane	3	10
Nitroethane	6	56
1-Nitropropane	10	44
2-Nitropropane	8	32
1-Nitro- <i>n</i> -butane	25	120
2-Nitro- <i>n</i> -butane	25	192
1-Nitro-2-methylpropane	20	164
2-Nitro-2-methylpropane	15	44
1-Chloro-1-nitropropane	50	Not gelled ^c
1,1-Dichloro-1-nitropropane	50	Not gelled ^c
2-Chloro-2-nitropropane	50	Not gelled ^c

^a 10 cc. of cement was used in each test.

^b The volume of the antigel was slightly less than that required to cause precipitation of the rubber.

^c After 1 month.

ACCELERATED GELLING TEST

It was obvious that storage at room temperature would require too much time before gelation occurred. In addition, room temperature varied too greatly with the seasons. Also, the compound given in recipe I proved slower in rate of gelling than was desirable, so a change in acceleration was made. Zinc dibutyl-dithiocarbamate is an ultraaccelerator, but to achieve faster action, polybutyraldehydeaniline was added to the mix. This cement gelled with commendable speed.

Room-temperature storage was still too slow, so the following technique was employed. A 25 × 200 mm. Pyrex-rimmed test tube was filled to about the three-

quarters point with the cement to be tested, loosely stoppered with a labeled cork stopper, immersed in a water bath, and maintained at $50 \pm 0.1^\circ \text{C}$ until gelling occurred, or until the test was terminated. The stopper was tightened after the contents of the tube had reached the temperature of the bath.

A temperature of 50°C was selected as high enough to give rapid gelling but not high enough to cause an excessive loss of solvent through the stoppers. The gelling time was taken as the period from immersion to the time the gel became too stiff to flow when the test tube was inverted (Table II).

EFFECT OF SOLVENT ON ACTION OF ANTIGEL

The concentrations of the antigel used in Table II were not directly comparable and obviously higher than was necessary for adequate protection; therefore in the following tests lower concentrations were adopted. Rubber cements

TABLE III
EFFECT OF SOLVENT ON THE GELLING OF VULCANIZING CEMENTS

Antigelling Agent	Benzene		Naphtha		Ethylene dichloride	
	Agent used (%) ^a	Hours to gel at 50°C	Agent used (%) ^a	Hours to gel at 50°C	Agent used (%) ^a	Hours to gel at 50°C
None	0	33.5	0	144	0	87
1-Nitro-2-methylpropane	1	39.5	1	132.5	1	96
	5	54	5	118	5	111
	10	57.5	10	108	10	Not gelled ^d
1-Chloro-1-nitropropane	1	63.5	1	201	1	Not gelled ^d
	5	162	5	Not gelled ^c	5	Not gelled ^d
	10	Not gelled ^b	10	Not gelled ^c	10	Not gelled ^d

^a Percentage by weight based on total weight of cement.

^b After 421 hours. ^c After 411 hours. ^d After 284 hours.

are normally prepared in benzene or naphtha, or occasionally in chlorinated solvents, such as carbon tetrachloride or ethylene dichloride. Tests were run on cements containing 10 per cent rubber made up in benzene, naphtha, and ethylene dichloride, respectively, according to the following recipe:

RECIPE II

	A	B
Rubber	100.0	100.0
Zinc oxide	10.0	—
Sulfur	5.0	—
Zinc dibutyldithiocarbamate	—	1.0
Polybutyraldehydeaniline	—	1.0
	115.0	102.0

The cements were made up to 10 per cent rubber concentration, and diluted to 5 per cent when tested. From the accelerated test results at 50°C , reported in Table III, it is evident that the cements containing 1-nitro-2-methylpropane

were protected only when benzene or ethylene dichloride was used as the solvent. 1-Nitro-2-methylpropane in a naphtha cement is a gelling agent. 1-Chloro-1-nitropropane is an active inhibitor of gelling in any of the various cements tested; it is particularly active in the ethylene dichloride cements.

Since many halogen derivatives of the nitroparaffins were available, they were tested as antigels for rubber cements. Table IV presents the results of tests in a benzene cement on these compounds and others of related structure. The cement was the same as that used in Table III, except that halogen derivatives of the nitroparaffins were substituted for the nitroparaffins and only in the benzene cement.

Any of the 1-chloro- or 1,1-dichloro-1-nitroparaffins tested are quite effective in cements with acceleration of this type. The compounds substituted in the 2-position are inferior to those substituted in the 1-position, although they possess definite protective qualities. The dichloro-substituted products are as good as

TABLE IV
EFFECT OF ACCELERATED STORAGE TEST ON HALOGEN-SUBSTITUTED
NITROPARAFFINS IN BENZENE

Compound	Percentage added	Hours to gel at 50° C
Blank	0	38
1-Chloro-1-nitroethane	0	Not gelled ^a
1,1-Dichloro-1-nitroethane	5	Not gelled ^a
1-Chloro-1-nitropropane	5	Not gelled ^a
1,1-Dichloro-1-nitropropane	5	Not gelled ^a
2-Chloro-2-nitropropane	5	80
2-Chloro-2-nitrobutane	5	74
1-Chloro-1-nitro-2-methylpropane	5	329
Chloroform	5	38
Carbon tetrachloride	5	38
Nitrobenzene	5	38

^a After 459 hours.

the monochloro-substituted. The failure of chloroform, carbon tetrachloride, and nitrobenzene to prevent gelling was as expected. In the remainder of the test, 1-chloro-1-nitropropane was used exclusively, as it was considered the best from many angles.

STORAGE AT ROOM TEMPERATURE

While it has been demonstrated that these materials are effective as antigels at temperatures quite out of normal storage conditions, reactions differ at different temperatures; therefore tests at room temperature were run (Table V). All samples were stored in screw-capped glass bottles in a cabinet maintained at $82 \pm 1^\circ \text{F}$ ($28 \pm 0.5^\circ \text{C}$).

The milling time, aging period before dissolving, and churning period were varied separately. Two types of rubber were used—a blend of plantation crudes for one series and sprayed-latex rubber for another. Some were milled 10 and some 15 minutes on a 6×12 inch laboratory mill, with a roll temperature of $140\text{--}150^\circ \text{F}$ ($60\text{--}66^\circ \text{C}$). The benzene used in this series was redistilled and dried over calcium chloride.

Table VI presents data showing the effect of various loading agents on the gelling of the cements and on the action of the antigel.

It is evident that many loading agents can be used in the presence of 1-chloro-1-nitropane. However, various tests indicate that strong bases form complex salts with the antigel and thus destroy the value of the cement. For example, diphenyl-

TABLE V
EFFECT OF VARIATION IN MILLING, AGING, AND CHURNING PERIODS
ON BENZENE CEMENTS

Milling time (min.)	Aging period (hrs.)	Churning period (hrs.)	Gelling time at 82° F		
			Blank (days)	1-Nitro- 2-methyl- propane (days)	1-Chloro-1 nitropropane
RUBBER BLEND					
10	0	24	4	8	5 mo. 11 days
10	0	24	4	8	Not gelled ^a
10	72	24	3	10	Not gelled ^a
10	72	24	3	10	6 mo. 10 days
10	0	48	5	10	6 mo. 0 days
10	0	72	4	9	3 mo. 13 days
15	0	24	6	11	6 mo. 0 days
15	0	48	5	12	4 mo. 10 days
15	0	72	4	11	5 mo. 9 days
LATEX-SPRAYED RUBBER					
15	0	24	11	31	Not gelled ^a
10	0	24	8	30	Not gelled ^a

^a After 6.5 months.

TABLE VI
EFFECT OF LOADING AGENTS ON ANTIGELLING ACTION

Rubber	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Sulfur	3	3	3	3	3
Zinc dibutyldithiocarbamate	0.5	0.5	0.5	0.5	0.5
Polybutyraldehydeaniline	0.5	0.5	0.5	0.5	0.5
Whiting	100	—	—	—	—
Magnesite	—	100	—	—	—
Lithopone	—	—	100	—	—
Titanium dioxide	—	—	—	100	—
1-Chloro-1-nitropropane	100	100	100	100	100

GELLING TIME AT 50° C

Without 1-chloro-1-nitropropane (hrs.)....	31	31	31	22	22
With 1-chloro-1-nitropropane (days).....	Not gelled ^a	16	35	51	Not gelled ^a

^a After 51 days.

guanidine cements cannot be cured because of this salt formation. Lime and magnesia combine with the antigel and thus prevent its exercising any inhibitory action.

The bonding power of the cements is not affected, although the rate of cure may be decreased somewhat by retention of traces of the antigel in the film.

TEST FORMULAS FOR RECLAIMED RUBBER *

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In 1934, Palmer³ presented a definite program for the testing of reclaimed rubber, in which it was stated that physical tests in a recipe containing reclaimed rubber were of definite value if they were known to have a direct and accurate interpretation in reference to tests on the finished product. This procedure was made secondary to an actual factory run with the reclaim mixed in typical compounds. In the latter case, of course, the tests may be run by the consumer of the reclaimed rubber, whereas in the former case they may be run either by the consumer or the manufacturer. It is the desire of the manufacturer to test his product in a manner which properly interprets it for the consumer. For this purpose, test formulas have been coming into fairly general use and, inasmuch as there are innumerable formulas which may be used, it is most desirable and essential to have some uniformity for the sake of universal comparison and simplicity of operation. It is the purpose of this paper to point out the greater uniformity of results obtained with compounded test formulas, and to make definite recommendations of several such formulas.

The ideal test formula should not only measure the uniformity of reclaimed rubber from lot to lot, but should also predict to some extent its performance when used in the consumers' products. Although the reclaim-sulfur mix is still used by many for this purpose, it is recognized by most reclaim manufacturers and many larger consumers that this formula gives erratic and undependable results. The reclaim-sulfur mix contains 100 parts of reclaimed rubber and 5 parts of sulfur, and is generally cured from 15 to 35 minutes at 141.7° C (287° F). Winkelmann⁷, Stafford⁶, Hurleston², and Palmer³,⁴ have either mentioned or protested the lack of correlation of the reclaim-sulfur test with the compounding value of the reclaim, and have pointed out the shortcomings of this test. It has been shown⁸ that the reclaim-sulfur test is accurate at best to only 10 per cent, and that even the best results are not a criterion of the properties of the reclaim in the recipe in which it is to be used. Maximum variations from 12 to 19.5 per cent of the mean in the tensile strength and from 10 to 11 per cent in elongation in the reclaim-sulfur mix were reported in 1940 by Palmer and Crossley⁵.

In contrast to the above inconsistencies, the variation involved in the use of a compounded test recipe is definitely less, as shown in Table I. These tests were run in test formulas IV and V (Table VII). Equal parts cut from three slabs of whole-tire reclaim A were thoroughly blended on the mill, and from this blend six mixes of each formula were made, two slabs from each mix were cured, and three strips from each slab were tested. All tests were made in accordance with the standard practice as recommended by the A.S.T.M.¹, except that the compounds were aged only 4 hours between mixing and curing. The maximum variations in tensile strength from test to test for formulas IV and V are 5.9 and 6.2 per cent of the mean, respectively, compared to 10, 12 and 19.5 per cent

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previously referred to for the reclaim-sulfur test. The maximum variations in elongation from test to test for formulas IV and V are 10.1 and 5.1 per cent of the mean, respectively, compared to 10 and 11 per cent previously reported for the reclaim-sulfur test.

Throughout this paper, the term "maximum variation from test to test" is used to describe the variation in physical properties of reclaimed rubber, rather than the more mathematically precise "root mean square error" or "standard deviation", because it is believed that the actual extent to which any one test might differ from any other is of more interest than a mathematical expression of the probable error of any one test. From the point of view of control testing, it is the extreme variations from test to test in the reclaim-sulfur mix which have been most confusing, and these extremes are not emphasized if the variations are expressed as "standard deviations".

TABLE I
VARIATION IN PHYSICAL TESTS OF TEST FORMULAS

Mix No.	Slab No.	Formula IV, cure 6 minutes at 158° C		Formula V, cure 12 minutes at 148° C	
		Elongation (%)	Tensile strength (kg. per sq. cm.)	Elongation (%)	Tensile strength (kg. per sq. cm.)
1.....	1	415	90.7	585	170.8
	2	410	88.6	600	172.2
2.....	1	410	91.7	590	171.5
	2	390	87.2	605	172.9
3.....	1	380	88.2	605	181.7
	2	375	87.9	600	175.1
4.....	1	395	91.0	585	175.8
	2	380	87.5	580	175.8
5.....	1	380	87.5	585	177.9
	2	395	92.4	575	176.1
6.....	1	410	91.0	585	175.4
	2	390	88.6	585	178.9
Average		394	89.4	590	175.3
Maximum variation		40	5.2	30	10.9
Per cent of average.....		10.1	5.9	5.1	6.2

As further evidence of the unreliability of the reclaim-sulfur test, a comparison was made of three typical reclaims in the reclaim-sulfur mix and in formulas I, II, and III (Table III). The characteristic analyses of the reclaims used are given in Table II. A and B are whole-tire reclaims, and C is a tube reclaim of neutral color, all of which are manufactured by the alkali digestion process.

Over a period of nine months, a considerable number of lots of each reclaim were tested, using a blend of five random samples from each lot for each test. Each blend was simultaneously tested in the reclaim-sulfur mix and in formulas I or II, as indicated in Table IV. There is up to three times as much variation in tensile strength and up to one and one-half times as much variation in elongation from test to test in the reclaim-sulfur mixes as in the corresponding test formula mixes.

In Table V a comparison has been made of the elongations and tensile strengths of the reclaim samples displaying the greatest variation in reclaim-sulfur tensile strength with the corresponding tests obtained when the same sample of reclaim is tested in formulas I, II, and III. The variations in reclaim-sulfur tensile strengths and elongations are large, and are not reflected in the

results obtained from the test formulas. Consequently, the reclaim-sulfur test cannot be used as an indication of reclaim quality.

These are only a few of the many instances of the unreliability of the reclaim-sulfur test which have been experienced. In most cases the variation in reclaim-sulfur tensile strength is not reflected in the final compound. However in cer-

TABLE II
ANALYSES OF RECLAIMS

Type	A	B	C
Color	Whole-tire Black	Whole-tire Black	Tube Neutral
Manufacturing process	All by alkali digestion		
Specific gravity (grams per cc.).....	1.15	1.15	1.25
Chemical tests			
Acetone extract	8.80	10.80	7.50
Ash	16.50	15.70	32.00
Total sulfur	2.10	1.90	2.10
Carbon black	12.70	14.50	0.70
Alkalinity (as NaOH).....	0.20	0.50	0.20
Rubber content (by difference).....	59.90	57.10	57.70

TABLE III
FORMULAS AND PHYSICAL PROPERTIES

Type	I Mechanical moulded goods	II Tire carcass	III Tire carcass
TEST FORMULAS			
Smoked sheet	10.00	—	31.62
Brown crepe	—	17.00	—
Reclaimed rubber	50.00	65.00	50.00
Zinc oxide	2.00	1.50	1.25
Natural whiting	15.40	9.62	12.00
Clay	20.00	2.00	—
Stearic acid	0.60	0.50	0.75
Pine tar	—	1.50	2.00
Sulfur	1.40	2.50	2.00
Diphenylguanidine	0.60	—	—
Mercaptobenzothiazole	—	0.38	0.38
	100.00	100.00	100.00

RANGE OF PHYSICAL PROPERTIES

Time of cure (minutes).....	6	25	25
Temperature of cure (centigrade)...	158	141.7	141.7
Elongation (per cent).....	385-435	485-535	600-650
Tensile strength (kg. per sq. cm.)...	70-100	105-135	140-170
Shore (Type-A) hardness.....	67-72	52-57	45-50

tain types of compounds where reclaim is the main ingredient, variations in tensile strength of reclaim in the reclaim-sulfur test may carry over to the compound, and show a trend, but the differences are not proportional to those observed in the reclaim-sulfur test.

Throughout this paper, tensile strength and elongation have been considered the criteria of quality by which a compound is judged. In some cases these

properties are not entirely indicative of the performance of the ultimate product, and it frequently becomes desirable to obtain tests which more nearly duplicate the service conditions of the final product. For example, such tests may be abrasion and flexing resistance, cold and hot compression-set, resistance to heat build-up, resistance to artificial aging, and many others, any of which may be

TABLE IV
RECLAIM-SULFUR MIX *vs.* TEST FORMULAS

Reclaim	Formula	Cure		No. of tests	Tensile strength				Elongation			
		Min.	Centi-grade		Max.	Min.	Av.	Variation % of average	Max.	Min.	Av.	Variation % of average
					kg. ps	sq. cm.	%		%	%		
A	Reclaim-sulfur	25	141.7	36	56.2	39.7	45.7	29	405	300	355	30
B	Reclaim-sulfur	25	141.7	57	91.4	56.2	69.6	51	470	360	405	27
C	Reclaim-sulfur	25	141.7	30	90.3	53.8	66.8	55	595	460	520	26
A	I	6	158	28	98.1	82.3	86.8	18	480	380	425	24
B	II	25	141.7	54	131.8	107.2	114.9	21	530	435	495	19
C	I	6	158	34	103.0	85.4	90.7	19	510	430	460	17

TABLE V
RECLAIM-SULFUR MIX *vs.* TEST FORMULAS

Reclaim	Formula	Cure		Tensile strength			Elongation		
				Sample having highest tensile	Sample having lowest tensile	Difference	Sample having highest tensile %	Sample having lowest tensile %	Difference %
		Min.	Centi-grade						
		(kg. per sq. cm.)							
A	Reclaim-sulfur I	25	141.7	56.2	39.7	16.5	405	320	85
		6	158	92.5	92.1	0.4	425	435	10
B	Reclaim-sulfur II	25	141.7	91.4	56.2	35.2	440	370	70
		25	141.7	128.7	115.2	13.5	480	505	25
B	Reclaim-sulfur III	25	141.7	82.6	52.7	29.9	685	440	225
		25	141.7	163.1	163.8	0.7	645	605	40
C	Reclaim-sulfur I	25	141.7	90.3	53.8	36.5	595	460	135
		6	158	92.8	91.8	1.0	460	460	0

obtained from test formulas, and which serve as definite indications of what may be expected in service, whereas such tests run on the reclaim-sulfur mix would have very little meaning. The authors do not mean to imply that the use of test formulas is the panacea to cure all testing ills, but it is believed that by their use the manufacturer and consumer of reclaimed rubber may more nearly approach the perfect test, which is, of course, an actual production trial in the consumer's factory, with service tests on the resultant product.

ACCELERATOR COMBINATIONS

It has been suggested^{3, 4, 5} that the most desirable test formula to use is one typical of that in which the reclaim will be used. For a routine production control test, however, this is not practical, as it would involve a great number of formulas and considerable laboratory work. Accordingly, it seems desirable to standardize on one or two simple formulas of general nature, which can be used to control the uniformity of all reclaims. Formula I (Table III) answers this requirement, except that reclaims having different rates of cure, when tested in this formula, fail to attain their optimum properties in the same curing time.

For example, a reclaim highly alkaline in reaction might reach its optimum cure in 5 to 6 minutes, whereas a neutral reclaim might require 8 to 10 minutes. Thus, it would be necessary to have a special cure for each type of reclaim. It seems desirable from an efficiency standpoint to standardize on one cure for all reclaims if possible, and, accordingly, a study was made of a number of different accelerator combinations in an effort to find one which would be flexible enough

TABLE VI
ACCELERATION FOR TEST FORMULA

Type of acceleration	Number of different reclaims tested	Number of reclaims reaching optimum properties at 158° C		
		4 min.	6 min.	8 min.
Diphenylguanidine	13	None	5	8
Dibenzothiazyl dimethylthiolurea ...	6	2	2	2
Zinc salt of mercaptobenzothiazole and di- <i>o</i> -tolylguanidine	4	None	4	None
		(All tensile strengths low)		
Dibenzothiazyl dimethylthiolurea and diphenylguanidine	13	2	10	1
Zinc salt of mercaptobenzothiazole..	4	None	2	2
		(All tensile strengths low)		
Benzothiazyl disulfide	7	3	2	2

to meet this condition. These results are shown in Table VI. The reclaims used in this work were typical of all the different types commonly produced. Although no one accelerator combination was found to be completely satisfactory, the combination of dibenzothiazyl dimethylthiolurea and diphenylguanidine appeared to be the best, since it showed 10 optimum tensiles at 6 minutes out of the 13 reclaims tested.

As only a few of the more common accelerator combinations were investigated, there are doubtless many others which would prove equally satisfactory.

RECOMMENDED FORMULAS

In Table VII are listed three test formulas which are recommended for testing reclaimed rubber. Formulas IV and V employ the dibenzothiazyl dimethylthiolurea-diphenylguanidine accelerator combination, and are suggested for routine control testing purposes to replace the reclaim-sulfur test. For simplification in handling, and for time and labor saving, the rubber and fillers in these formulas can be master-batched, so that it is only necessary to weigh reclaim and master batch for the final mix. In some cases, it might be desirable also to omit the sulfur from the master batch and add it to the final mix; in this case, three weighings would be required, compared to two weighings for the reclaim-

sulfur mix. If the master batch method is used, the final mix can be made in 5 to 6 minutes, and this compares favorably with the time required to mix a reclaim-sulfur batch. The curing time for the test formulas (6 to 12 minutes) is less than for the reclaim-sulfur mix (generally 15 to 35 minutes). The point to be emphasized here is that in replacing the reclaim-sulfur test with a compounded test formula, there need be no increase in the time and labor of testing.

Formula III (Table III) and formula VI (Table VII) are suggested at typical of compounds to be used in testing reclaims for use in carcass or tread compounds. Various tests may be obtained, such as stress, elongation, tensile strength, hardness, artificial aging, abrasion and flexing resistance, and any others which aid in predicting the performance of the reclaim in service.

TABLE VII
FORMULAS AND PHYSICAL PROPERTIES

Type	IV General purposes moulded goods	V	VI Tire tread
TEST FORMULAS			
Smoked sheet	10.00	36.00	36.00
Reclaimed rubber	50.00	50.00	40.00
Zinc oxide	2.00	3.30	2.50
Clay	20.00	4.00	—
Whiting	15.30	2.60	—
Carbon black	—	—	17.70
Stearic acid	1.00	1.30	1.70
Sulfur	1.40	2.31	1.75
Mercaptobenzothiazole	—	—	0.35
Diphenylguanidine	0.10	0.16	—
Dibenzothiazylidimethylthiolurea ...	0.20	0.33	—
	100.00	100.00	100.00
RANGE OF PHYSICAL PROPERTIES			
Time of cure (minutes).....	6	12	35
Temperature of cure (centigrade)...	158	148	134.5
Elongation (per cent).....	375-425	575-625	550-600
Tensile strength (kg. per sq. cm.)...	70-100	160-190	195-225
Shore (Type-A) hardness.....	70-75	48-53	65-70

At the request of the consumer, the manufacturer can and does test reclaimed rubber in a specific test formula which the consumer may submit for this purpose. On the other hand, the consumer may agree to be guided by the results of tests from a test formula suggested by the manufacturer. It is hoped that the suggestion of formulas IV and V particularly, as well as formulas III and VI, will aid in the development of this more practical method of testing reclaimed rubber.

CONCLUSIONS

The maximum variation from test to test obtained when testing a sample of reclaimed rubber in compounded test formulas is approximately half that experienced when the reclaim-sulfur test is used.

When tested with sulfur alone, reclaimed rubber may show a widely varying tensile strength and elongation from lot to lot, whereas much less variation in results is observed if the reclaimed rubber is tested in a compounded formula.

For this reason, and also because the results obtained are more indicative of final performance, test formulas of a general nature are preferable to the reclaim-sulfur test.

When test formulas are used in preference to the reclaim-sulfur mix, there is no increase in the work of testing.

A combination of dibenzothiazyl dimethylthiolurea and diphenylguanidine gives very satisfactory results for most types of reclaim.

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A METHOD FOR THE TESTING OF ADHESIVE TAPE *

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In the course of a study in the laboratory of the senior author, at Ithaca, N. Y., of pressure-sensitive adhesives, the authors became convinced that none of the generally accepted methods for the testing of insulating tapes was accurate enough to be a reliable measure of the quality of masking tapes. The appended references are to those more recently published articles which describe methods in current use for the testing of rubber tape, and are included here merely for the sake of completeness. In our studies, the very irregular results which we found seemed to reside partly in how the test-specimens were prepared, and partly in the apparatus used. After a long examination into the requirements, it became clear that accuracy could be obtained only by the use of apparatus which was designed specifically for the purpose of these tests, and by the application of precise manipulative methods.

The purpose of this paper is to present a brief description of the apparatus and the methods used, in the hope that it may be of interest, not only to those who test masking tape, but also in the field of testing of rubber insulating tapes. The specific materials tested under these procedures were cloth-backed industrial adhesive tape and paper-backed masking tape. They were received in rolls 1 inch wide and 50 feet long. The adhesives tested were pressure-sensitive ones, containing rubber as the basic ingredient. The room in which the tests were performed was small and, by means of an air-conditioning unit designed for this room, the temperature was maintained at $70^{\circ} \pm 2^{\circ}$ F throughout the 2 years of the study. The humidity was also controlled at 55 ± 5 per cent.

MATERIALS USED

For certain of the tests, strips of sheet steel, 2 by 8 by 0.019 inches were used. Each metal strip was gaged with a micrometer in six places, and any which varied more than 0.001 inch were rejected. They were then lacquered with Duco lacquer and polished by a professional finisher of automobile bodies. The lacquered strips were cleaned by swabbing with 1-inch squares of surgical cotton dipped in chemically pure carbon tetrachloride. The cotton was manipulated with forceps, so that at no time was it touched by hand. The metal strips at all times were handled by the edges. After cleaning, they were lightly brushed with a clean piece of bleached muslin to remove fibers left from the cotton. No cotton or muslin pieces were reused.

To set up these metal strips for application of the tape, two of them, held by the edges, were placed on the ruled board of the tape cutter, Figure 2, and marked with a red pencil along one side of the strip at 1, 2, and 6 inches from the right-hand end. They were then set in position on the surface plate, *H*, of Figure 1. At each end of these strips, fastened to the surface with tape, was a

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blank half strip of lacquered metal to maintain a constant level for the roller throughout its journey across the surface plate. The rolling machine was thus made ready for the tape. This machine is described later.

To prepare the tape samples, a roll of tape was placed on the spool of the tape cutter, Figure 2, so that the tape could be unrolled with the backing side down. Six feet of tape were cut from the roll and rejected. The balance of the roll was then ready for immediate use. Mounting blocks, shown in Figures 2 and 3, are provided to insure attachment of tabs without contamination of the tape samples.

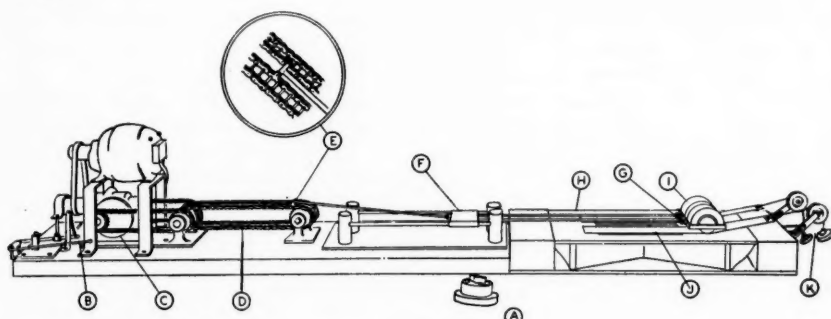


FIG. 1.—Rolling machine.

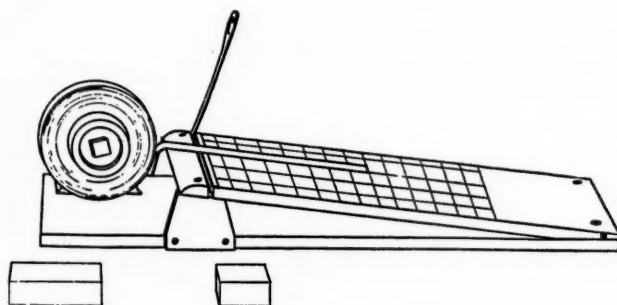


FIG. 2.—Tape cutter and blocks.

A paper tab, 1 by $7\frac{1}{4}$ inches, provided with a strip of aluminum 1 by $\frac{3}{8}$ inch pierced by a $\frac{3}{16}$ -inch hole fastened at one end of the paper tab by means of a small piece of industrial tape, was set on the mounting block. A 13-inch strip of tape was cut from the roll, using the tape cutter, Figure 2, the tape being removed from the roll at the rate of 6 inch per second. It is important to observe this exact rate. The test-piece of tape was picked up by the ends, turned adhesive-side down, held free from any contacts until the 4 inch of tape at the right end of the strip were fastened to the paper tab. The specimen with attached tab was removed to the surface plate, and 1 inch at the left end of the tape was fastened to one of the blank metal strips, across the division, and to the left end of the corresponding test metal strip. By means of a hook and cord passed over a pulley, a 100-gram weight was fastened to the tab at the right end of the tape, see Figure 3. The samples were then ready for rolling into contact with the lacquered metal.

ROLLING MACHINE

It was found by long and careful experiment that the measured adhesion shown by a given roll of tape varied greatly when the tape specimen was applied to the metal strip by other than precise methods. The purpose of the rolling machine was to roll down the tape samples upon the lacquered metal strips uniformly so that each tape sample was applied to its particular strip under exactly duplicated conditions as to time and pressure.

The rolling machine consisted of three basic parts: (1) a surface plate; (2) the roller with its frame and weights, and (3) the chain drive for the roller. The surface plate had the usual accuracy of flatness to be expected from such an article. This was tested by means of a spherometer, and the one used was found to conform to high accurate uniformity of flatness of surface. The roller consisted of a steel cylinder 2 inches in diameter by 8 inches long, mounted in a frame upon which were two lead weights arranged to be moved by a motor and chain mechanism at a uniform rate of $4\frac{1}{2}$ inches per second to and fro across the 9 by 14-inch surface plate. The roller and lead weights together gave a load of $8\frac{1}{2}$ pounds per inch width of tape. The roller was turned, ground, and polished with an accuracy equal to that of the surface plate. It was then chromium-plated and regaled.

Reference to Figure 1 will show the relations of the several parts of the rolling machine. A is the main switch, H the surface plate, and I the roller with frame and weights. It will be observed that two test-specimens are rolled simultaneously, although one may be a dummy. This is necessary in the interest of uniformity because no scheme of rolling a tape as narrow as 1 inch wide gives a uniform distribution of weight. Even with rolling two at once, a necessary feature of the mechanism is a two-directional joint G, which permits the roller to move over irregularities in a direction perpendicular to the direction of travel of the roller and, also, in a direction at an angle to the plane of the surface plate. The necessity for this is that tape is highly accurate as to thickness. The parallel rods and carrier F insure exactness of the horizontal direction of motion of the roller. Because uniformity of motion over the tape being rolled was found necessary, due to the influence on the adhesion of any dwell upon any given portion of the tape, a chain drive, D, for the roller mechanism was developed. E shows the attachment of the connecting rod to the chain; B is a brake which is necessary to stop the roller at a specific place; C is the speed reducer for the motor.

It is to be noted, from the arrangement of the test plates, tape weights, and pulleys, J and K, that the adhesive on the tape at no time came in contact with the metal to which it was to be applied, until brought in contact with it by the motion of the roller. This is important. Figure 3 shows this condition more in detail. This shows the surface plate, roller, metal strips, and tape in position; also the blocks diagrammatically shown in Figure 2 which are used to prevent contamination of the adhesive when applying the tape specimen to the tabs.

Two 13-inch strips of tape are cut, mounted on the tabs, and fastened in the outer position on the rolling machine in the manner already described. The two test-pieces of tape, when ready to be rolled down on the lacquered metal strips, are set up as in Figure 3. The roller passes lengthwise over the tape a total of six times, three times in one direction and three times in the opposite direction. By means of the brake, B, Figure 1, the roller can be stopped in position off the metal strips at the left.

When the rolling is finished, the weights are unhooked from the tabs, and the tape and metal strips removed from the surface plate. The $\frac{1}{2}$ inch of tape at the left which overlapped the blank metal strip is folded back and fastened to the underside of the lacquered metal strip. The strips are then set aside to stand for 15 minutes before testing.

THE TESTING MACHINE

The stripping test machine is shown in Figure 4. Essentially, the machine is an adaptation of a Scott yarn testing machine. Duplicate jaws are used, so that two pieces of tape can be tested simultaneously. By means of reducing gears, the speed of the jaws is brought to 13 inches per minute. The two jaws are attached on one threaded shaft driven by a reversible motor so that the jaws can be lowered during the test and raised to the original position after the test at the same rate (13 inches per minute).

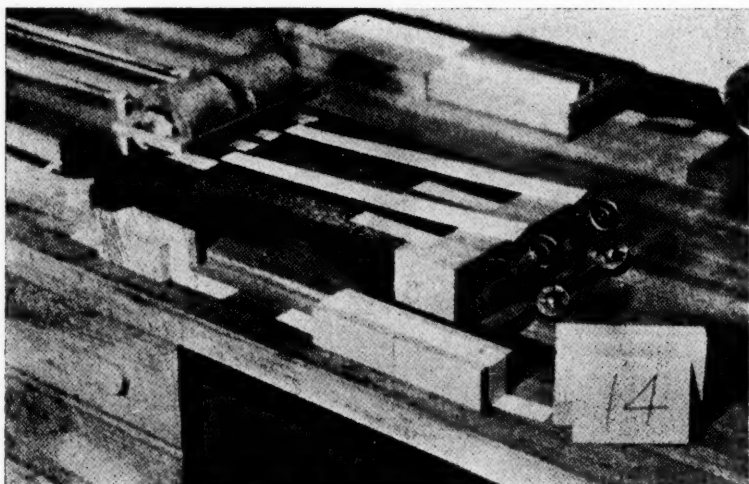


FIG. 3.—Roller ready for use.

The autographic record is drawn on a chart fastened to the drum of a Phipps & Bird Kymograph, the drum of which revolves at the rate of 4 inches per minute. The rate of rotation of the Kymograph is not pertinent, although the speed selected was that which would show a reasonable relation to the actual amount of tape stripped from the metal. In practical use, the speed may be greater or less at the desire of the operator. Thus, he could show on a given chart fewer or more individual tests.

To measure the adhesion it was found, after much study, that a push-pull spring balance was the most accurate and most satisfactory means of applying the load. They were made by Chatillon to special design. A light-weight holding device was attached in place of the usual pointer. This carried an arm of spring steel and a pen, light enough in weight so as to be well within the load tolerance of the spring balance. The spring balance was fixed upon a bracket and positioned so that the pull would be exactly vertical. Spring balances of the customary friction-bearing type were wholly unreliable. Therefore, the ones used were made with ball bearings at top and bottom, and even these needed

to be adjusted with extreme accuracy, and the axis of the rod through the balance was made to pass through the exact center of each of the ball bearings. The balances were calibrated frequently by dead weights. Typical calibration charts, taken both by addition and reduction of load, are shown in Figure 6.

The charts used for these tests were 6 by 20-inch pieces of thin semi-transparent paper, on which horizontal lines corresponded exactly with the scale markings on the balance. For the 18-ounce balance the chart was ruled in ounces. For the 5-pound and 10-pound balances the chart was ruled in quarter and half pounds, respectively, the same chart having been used for either balance. Along the bottom of the charts were spaces for the usual records.

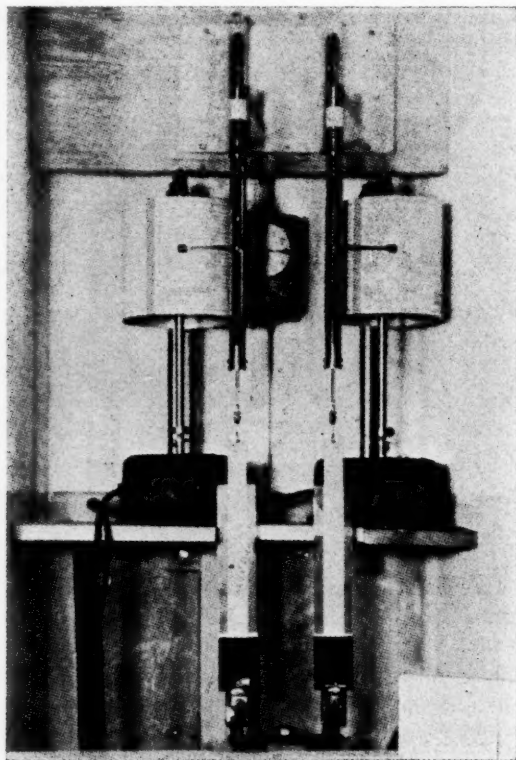


FIG. 4.—Push-pull spring balance.

The actual method for performance of the test is as follows:

After the tape is rolled on the metal strip, it remains undisturbed for 15 minutes \pm 10 seconds. Then the tab of the test-piece is doubled back over the tape, and the tape stripped by hand up to the first red mark 1 inch from the right end of the metal strip. The end of the metal strip thus uncovered is clamped in the jaw of the testing machine so that the strip is in a vertical position, the tab having been lined up directly in front of the tape. The hole in the upper end of the tab is slipped over a hook at the lower end of the spring balance. Every motion of the operator must be timed to duplicate the set-up for each test.

The other test-piece is set in position under the second spring balance. When the tape is stripped from the metal piece, the rough paper or cloth backing of the specimen which is still on the metal may rub against the back of the part already being pulled off. The friction thus induced may cause errors in the record. To avoid this, a piece of waxed paper 2 by 8 inches is placed between the tab and the tape. Thus, the rough back may rub against this waxed paper, and experience has shown that the errors due to friction are eliminated.

The chart is adjusted to zero, and the drum rotated to give a $\frac{1}{2}$ -inch zero line. The drum is stopped, and the jaw started downward. The tape is allowed

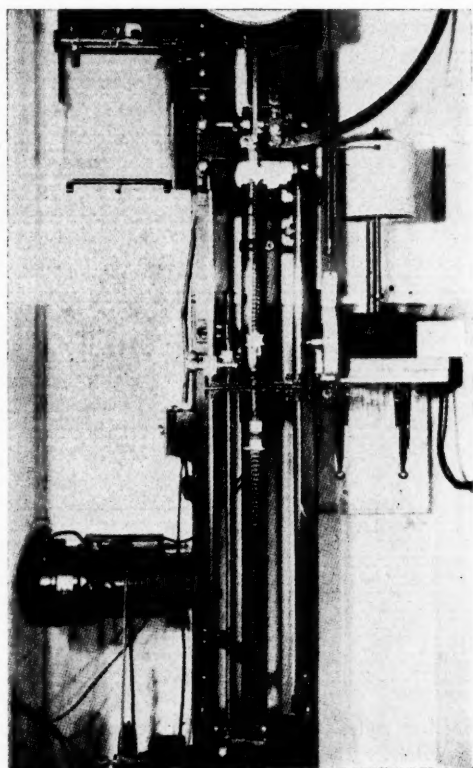


FIG. 5.—Test adaptation to Scott machine.

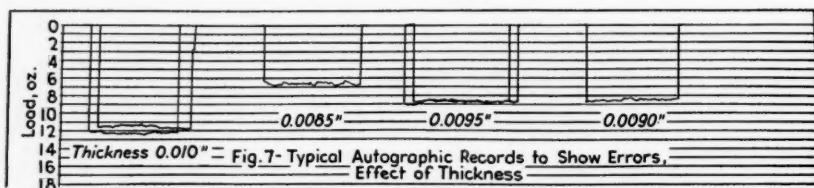
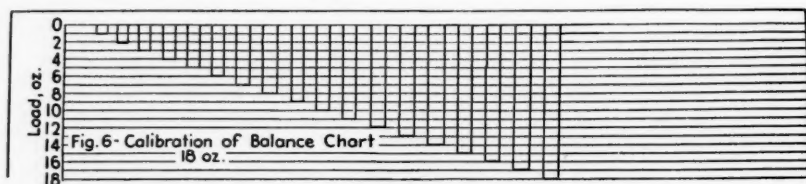
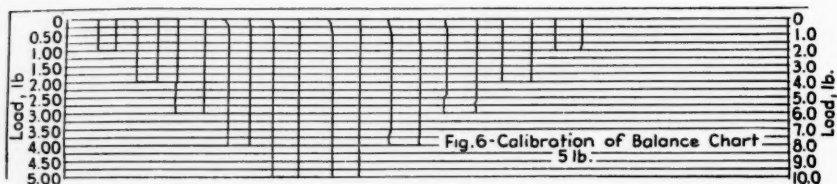
to strip up to the second red mark, 2 inches from the lower end of the lacquered metal strip. At this point the drum is started, and an autographic curve of the force required to strip the tape from the lacquered metal is recorded.

When the tape has stripped to the third red mark, 6 inches from the lower end of the metal strip, the drum is stopped. This gives a curve which corresponds to 4 inches of stripping under uniform conditions. The jaw motion is reversed, the balance is allowed to return to zero, and a second $\frac{1}{2}$ inch zero mark is recorded by running the drum for a short time. Thus, a record of accuracy of the spring balance and of the setting of the machine is recorded for each test made. The strips are then removed from the machine.

If reference is now made to any one of the records on Figure 7, it will be seen that the vertical line indicates the increase of tension until the tape begins to strip from the lacquered metal. From then on, the line is irregular in a horizontal direction, and shows the value of the adhesion between tape and lacquer.

In performing this test, rolling one pair of test-pieces and stripping another pair which had remained undisturbed for 15 minutes \pm 10 seconds may be alternated so that the testing may be performed without delay through a given series of tape samples.

For measurements of other qualities of the tape, such as the anchorage of the adhesive mass to the paper or cloth backing or the adhesion of the mass to the back, a similar technique may be employed.



Stripping from the full roll is performed by the use of a Scott rubber testing machine, the jaw of which is modified by the addition of a metal cylinder 1 inch wide and of a diameter to fit inside the cardboard spool of a roll of tape snugly enough to prevent the spool from slipping on the cylinder. The cylinder is mounted in such a way that it can be revolved freely on its axis; see Figure 5.

The set-up consists of a Chatillon push-pull spring balance and a Kymograph like those which have been described above. The jaw of the machine is lowered at the rate of 25½ inches per minute.

Six feet of tape are cut from the roll and rejected. The roll is placed on the metal cylinder of the test machine so that when the tape is pulled upward from the roll, the back of the tape is toward the operator. A 5-inch length of tape is stripped from the roll. A metal tab 1¼ by 2¾ inches punched at one end, is fastened to the adhesive 1½ inches from the end of the tape, the punched end of the tab being toward the end of the tape. The 1½-inch end of the tape is folded over the tab and fastened.

A hole is punched in the tape, coinciding with the hole in the tab. On the back of the tape on the tab is written the tape sample number and the roll number. At the juncture between the loose end of the tape and the roll, a red pencil mark is made both on the roll and on the back of the loose end of tape, thus marking off one complete revolution of the tape on the roll. The hole of the tab is slipped over the hook on the bottom of the spring balance.

The chart is adjusted to zero, and the drum rotated to give a $\frac{1}{2}$ inch zero line. The drum is stopped and the jaw started downward. As soon as stripping begins, the drum is started and an autographic curve of the force required to strip the tape from the roll is recorded.

When the tape has been stripped to the second red mark, that is, one complete revolution of the roll, the drum is stopped. The jaw is raised, the balance is allowed to return to zero, and a second $\frac{1}{2}$ inch zero mark recorded by running the drum for a short time. The test-piece is cut from the roll and the tab removed. In performing this test, one roll is prepared and tested at a time.

RESULTS

A very large number of tests were performed on metal strips lacquered with Duco and other types of automobile finishes. Surfaces such as spring steel, cold-rolled steel, chromium plate, glass, and others were studied. Also the effect of roughening the surface with sandpaper and the effect of different methods of cleaning the strips were tested. A discussion of these variables, however, would require an inordinate amount of space. Therefore, only certain results with adhesion to lacquered metal have been reproduced. These have been selected to illustrate not only typical curves but also to show the effect of some factors which influence the adhesion to the most pronounced degree.

Figure 7 shows records in which the effect of the thickness of paper-backed masking tape against a Duco lacquer metal strip is recorded. The paper itself was 0.007 inch thick, so the thickness of the adhesive may readily be calculated. The thicker the adhesive mass, the higher the adhesion.

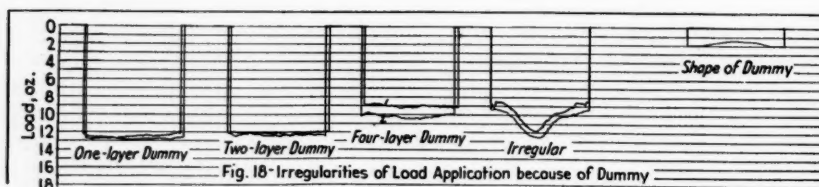
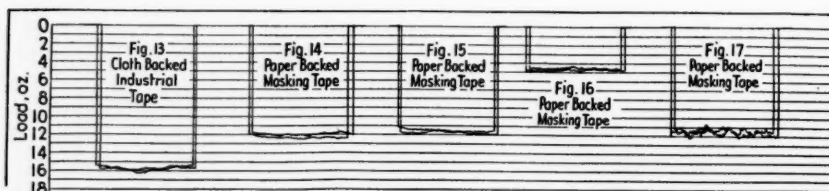
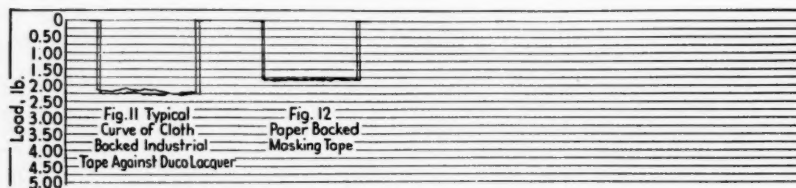
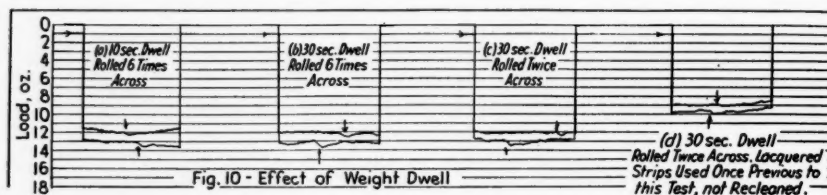
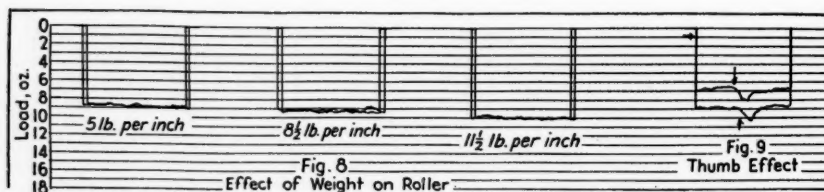
The weight on the roller was varied and the effect is shown in Figure 8. In this instance, the heavier the weight, the higher the adhesion. In the case of masking tape, which was known to be irregular of face, this merely means that there was a larger area of contact of the adhesive to the lacquer.

Figure 9 is interesting in that these two tape samples were rolled not with the roller, but by the usual method of rubbing them down with the thumb. The irregularities are not only over the entire distance of stripping, but also the higher adhesion when the thumb was allowed to dwell for an appreciable length of time on part of the tape.

Figure 10 shows the effect of dwell; namely, stopping the roller at a specific point on each of the samples tested, as is shown, for 10 seconds in one instance and 30 seconds in others. It was results of this sort which influenced the design of the rolling machine, Figure 1, for it proved the necessity of uniformity of application of load from end to end of the strip.

Figure 10(d) indicates also how the adhesion is reduced by minor impurities on the surface of the lacquer. In this particular instance, the lacquered strips had been previously used, but had not been recleaned.

Figure 18 demonstrates the influence of irregularities of load application. Such tests as these afforded evidence which led to the procedure of always rolling two strips of tape simultaneously, and these two strips of tape being from the same



roll and applied on lacquered metal strips of accurately gaged and identical thickness.

To insure uniformity of pressure of the roller over the tape width, two specimens are always rolled at the same time. In Figure 18, the word "dummy" is used merely to indicate that one or more layers of masking tape were used on lacquered metal strips in place of a regular strip of tape made up for testing. Thus, if the dummy is of one layer only, we get the first curve at the left. When of two layers, the adhesion is somewhat less, although the duplicates are somewhat irregular. When in four layers, the adhesion and the duplicates are not only less, but differ from each other. When a dummy or any strip of tape is used, the thickness of which is greater or less than that of the test-specimen, the roller rides at an angle on the test-specimen. The pressure, therefore, is not uniform over the width of the tape under test, and the curve does not record a true measure of the adhesion. In the case of the fourth curve, a specifically irregular dummy was cut to the shape shown, with the result that the adhesion curve shows somewhat the inverse shape of the dummy.

Because this paper primarily is a description of method and apparatus, only a few copies of curves drawn by tape tested under these conditions are included. The figures mentioned in the following paragraphs are copies of curves selected from a very large number. The discussion of them is necessarily brief.

Drawn on the 5-pound scale, Figures 11 and 12 are curves of cloth-backed industrial tape and paper backed masking tape.

Figures 13 to 17 are records of adhesives against Duco lacquered metal strips. The chart and spring balance used were of the 18-ounce scale. The kind of backing is indicated on each figure.

Figure 13 is a standard cloth-backed industrial tape, although it was spread with a different adhesive than that shown in Figure 11.

Compare Figures 13, 15, and 17, which show not only the number of ounces of pull required to strip these tapes, but also the uniformity or the irregularity of the curves. When the thickness was the same, we found that each adhesive drew a characteristic curve.

Of particular interest to the authors was a long series of tests of paper-backed adhesive masking tapes after they had been run under specific and uniform conditions of aging. Some rolls were aged in a dry oven and others in a humid oven. By the application of these methods and apparatus, it was possible to appraise the expected life of tapes of different construction and which used adhesives of different compositions.

CONCLUSIONS

The authors performed several thousand tests upon adhesives of different compositions, manufactured under excellent controlled factory conditions and carried upon backs of a variety of constructions. One conclusion was clear, which is included here even though this particular paper is devoted largely to a description of the test procedure alone. This is that other things being the same (paper or cloth of the same construction, methods of manufacture, and so on) each adhesive, when tested as described, gives a curve which is characteristic of its composition.

ACKNOWLEDGMENTS

The authors wish to acknowledge the coöperation of Anthony Hunt, who was an assistant in the laboratory and who performed by far the majority of the

tests. We would like to thank the officials of Johnson & Johnson, of New Brunswick, N. J., for whom the work was done, not only for their uniform coöperation, but for permission to publish this paper.

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APPARATUS FOR MEASURING SLOW RATES OF CONSUMPTION, OR EVOLUTION, OF GAS IN A CLOSED SYSTEM *

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The National Physical Laboratory was asked, in 1937, to obtain data on the aging of a few rubber samples by some test that did not involve heating to the relatively high temperatures used in the well-known Bierer-Davis bomb or Geer oven test. Reference to the literature suggested that volumetric measurement of oxygen absorption might be made sufficiently sensitive to allow discrimination between different grades after samples had been heated in oxygen at 50° C for one or two days. The apparatus described below was devised and the required tests were made, confirming the utility of the method. A paper by Milligan and Shaw appeared shortly afterwards (*Proc. Rubber Tech. Conf. London 1938*, 537), correlating the absorption by rubber of oxygen from air with changes in tensile properties. Although their procedure may be more suitable for routine testing of rubber, our apparatus is not only more sensitive, but may, perhaps, find application by other workers interested in small absorptions or evolutions of gas, particularly at temperatures other than atmospheric. This note, therefore, gives a description of the method used, and includes formulas for the calculation of the mass absorbed.

PRINCIPLE OF THE METHOD

If a manometer open to the air on one side is used to follow the changes in pressure in a closed system at atmospheric temperature, the readings will naturally vary with the temperature and pressure of the air, so that calculation is necessary before any absorption can be detected. A more serious inconvenience is that if the temperature of test differs considerably from that of the room, the travel of the manometer liquid increases from this cause alone, and may make the length required prohibitive unless various precautions are taken. By attaching to the "open" arm of the manometer a bulb similar to that enclosing the sample, it is possible to avoid both these troubles, and to reduce the precision required in the adjustment of temperature, since the readings become independent of temperature, to a first approximation. Oxygen was used in contact with the rubber, giving, presumably, some five times the rate of absorption occurring with air at the same temperature, and, since the apparatus was sealed off at about 18° C and heated to 50° C, there must have been a further increase in pressure of some 10 per cent. Milligan and Shaw introduced phosphorus pentoxide to absorb any moisture produced by the oxidation; we used soda-lime, which, though less effective in this respect, would remove carbon dioxide also, which has been stated to be formed in some cases, and might, it was hoped, reduce the rate of fouling of the mercury meniscus.

* Reprinted from the *Journal of the Society of Chemical Industry*, Vol. 60, No. 6, pages 171-173, June 1941.

APPARATUS

Two similar cylindrical bulbs (I and II), about 2.2 cm. in diameter and 10 cm. long, are connected at the top by a long piece of tubing of about 4.5 mm. bore, which is bent as shown in Figure 1 to form a differential manometer. The manometer arms are in the same plane as the axes of the bulbs, and the outer arm is continued vertically above the T-joint leading to bulb I: the manometer is spaced some 7 cm. away from the nearer bulb, so that it may remain outside

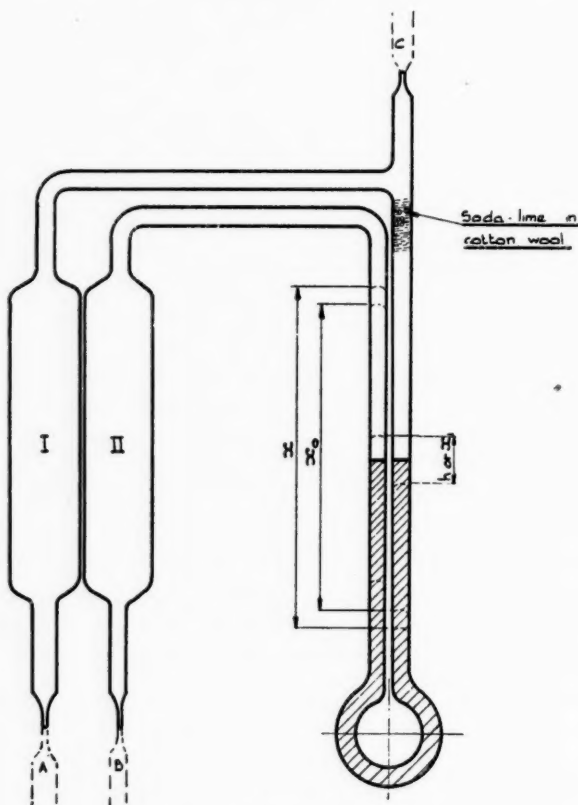


FIG. 1.

a thermostatic bath in which the bulbs are to be immersed. Bulbs I and II are drawn down at the lower ends and sealed to tubes of about 7 mm. and 3 mm. bore, respectively. A convenient support is provided by a third tube of the same diameter as the bulbs, open at the top and closed at its lower end, to which they are bound with nickel wire; if the bulbs have been arranged to lie in contact and the walls are reasonably straight, the assembly is rigid and unstrained. The open tube serves to hold a label, and is clamped above the water-level when the bulbs are submerged. The apparatus is cleaned with chromic acid solution and washed, and a measurement is made of the volumes of water that fill each bulb and the connecting tube as far as a datum line on the manometer; the average area of cross-section of the manometer arms may be determined at the same time.

METHOD OF USE

The rubber under test is cut up into shreds about 2 mm. square, and is introduced via A into bulb I. It was found that 15 grams, made up of 300 to 400 shreds, could be accommodated; the effect of the state of division has not been studied, but is probably not important for the rates of absorption that occur with rubber at 50° C. Dry air is passed through the apparatus from B to A, the opening at C being closed by a rubber tube and plug. The manometer is next charged with mercury, introduced through C by means of a drawn-out tube; a pledget of dry cotton-wool and a few grains of soda-lime wrapped in cotton-wool are pushed just past the T-joint. Bulb II is then sealed off at B; during the process the level of the mercury in the left arm of the manometer is sucked up nearly to the bend so that as much travel as possible may be available during calibration and absorption. A bulb of known volume, or a-burette, full of mercury is attached at A and a stopcock at C, and the apparatus is kept in an enclosure protecting it from draughts; the temperature θ and barometric pressure B are noted, and the readings of the manometer are taken before and after known volumes of mercury have been run out. These data are to provide a factor for the reduction of the volumes of oxygen absorbed to n.t.p. and a value for the free space in bulb I. When the calibration is finished, the mercury bulb is removed, and oxygen is passed from C to A to sweep out the air; tube A is sealed, and the final seal is made between C and the T-joint. Note is taken of the volumes of the glass tubing and rubber connections removed, which were included in the volume measured during calibration. The operations described have left bulb II filled with a known mass of air, and bulb I with rubber plus a mass of oxygen, which may be calculated from a reading of the differential manometer taken when both bulbs are at the same temperature. To minimize errors due to temperature differences, the definitive manometer readings are taken while the bulbs are immersed in water at about the temperature of the room. The bath is then heated to 50° C (controlled by thermostat) for a suitable period; the progress of the oxidation may be followed roughly by noticing the changes in reading while the bulbs are warm, but the readings used for calculation of the absorption are taken after standing overnight at room temperature. It may be pointed out that the actual value of the temperature has no effect on the manometer reading, provided that there are no differences in temperature between different parts of the apparatus.

CALCULATION

(a) *Determination of the free volume of bulb I.*—Suppose that the mercury level in the manometer stands x cm. higher in the arm connected to bulb II when, during the calibration, the other arm is open to the atmosphere at C. Let the free volume (total volume V_1 after sealing minus volume of rubber) of bulb I be V_1^1 and the volume of bulb II be V_2 , both measured to the surface of the mercury when the levels are equal; let Δ be the sum of the volumes between the burette and the seal made at A and between the stop-cock and seal at C, and let a be the area of cross-section of each arm of the manometer. The volume of air in bulb I and connections is therefore $V_1^1 + \Delta + \frac{1}{2}ax$ at the beginning of the calibration, and the volume in bulb II and connections is $V_2 - \frac{1}{2}ax$. The barometric pressure being B cm., the pressure in bulb II is $B - x$ cm. Now let the cock at C be closed, and when a volume y of mercury is run out of the burette attached to A, let the mercury meniscus in

the arm of the manometer connected to bulb II be h cm. above that in the other arm. (If the volume y has been suitably chosen, h will be of the same order as, but of opposite sign to, x .) The volume of air in bulb II has then increased to $V_2 - \frac{1}{2}ah$, and its pressure decreased to $(B-x) \times (V_2 - \frac{1}{2}ax) / (V_2 - \frac{1}{2}ah)$. The volume on the bulb I side has increased to $V_1^1 + \Delta + \frac{1}{2}ah + y$ and the pressure is h cm. more than that in bulb II. Hence, if the mass and temperature of the air have remained unchanged:

$$\frac{B(V_1^1 + \Delta + \frac{1}{2}ax)}{V_1^1 + \Delta + \frac{1}{2}ah + y} = \frac{(B-x)(V_2 - \frac{1}{2}ax)}{V_2 - \frac{1}{2}ah} + h$$

To find $(V_1^1 + \Delta)$ from this equation, it may be reduced to the form:

$$(V_1^1 + \Delta + y + \frac{1}{2}ah) / B = y - \frac{1}{2}a(x-h) / \{ (x-h)(1+f) \},$$

where $f = \frac{1}{2}a(B-x) / (V_2 - \frac{1}{2}ah)$ and values of V_2 and a have been obtained during preliminary measurement of the assembly. In many cases it may be possible to deduce a sufficiently accurate value of V_1^1 from the determined volume of bulb I and connections and the density of the weighed sample; the manometric calibration is not then necessary, but simultaneous values of B , x , and θ will still be required.

(b) *Determination of the mass of oxygen absorbed.*—Owing to cooling of the glass after the final seal has been made at C with bulb I full of oxygen, the manometer will probably not read exactly x cm. at the beginning of the absorption test. In our experiments, in which the oxygen pressure was made approximately atmospheric at the moment of sealing, and the tube had previously been drawn down to a short capillary for convenience, the fall in pressure was about 1 cm. If the new reading be x_0 , the oxygen pressure B_0 in I will be given by: $B_0 = x_0 + (B-x)(V_2 - \frac{1}{2}ax) / (V_2 - \frac{1}{2}ax_0)$. When oxygen equivalent to a certain volume v , measured at the pressure B_0 and at the same ambient temperature θ , has been absorbed by the rubber, so that the manometer reading is x_1 (which will assume a negative value when the process has passed the stage at which the mercury has become level in both arms), the pressure of air in bulb II will have fallen from $B_0 - x_0$ to $(B_0 - x_0)(V_2 - \frac{1}{2}ax_0) / (V_2 - \frac{1}{2}ax_1)$. The pressure in bulb I being x_2 more than that in bulb II, we have:

$$\frac{(V_1^1 - v)B_0}{V_1^1 + \frac{1}{2}ax_1} = \frac{(B_0 - x_0)(V_2 - \frac{1}{2}ax_0)}{V_2 - \frac{1}{2}ax_1} + x_1$$

This equation may be reduced to:

$$\frac{v - \frac{1}{2}ax_1}{V_1^1 + \frac{1}{2}ax_1} = \frac{x_0 - x_1}{B_0} \left\{ 1 + \frac{1}{2}a \frac{B_0 - x_0}{V_2 - \frac{1}{2}ax_1} \right\}$$

The volume v , obtained from this equation by inserting the observed values of B , x , x_0 , and x_1 and the value of V_1^1 calculated as in (a), is assumed measured at a pressure B_0 and temperature θ . The volume at n.t.p. and, hence, the mass of oxygen absorbed, is obtained by applying the appropriate factor.

RESULTS

Detailed figures for the rates of absorption of oxygen will not be given, as no adequate information is available regarding the samples tested. The order of rate that may be expected in the testing of rubber may be gathered, however, from the fact that the masses of oxygen absorbed per 100 grams of shredded

rubber varied from 8.9 mg. to 49.3 mg. in 15 hours at 50° C. These values corresponded to differences of readings of the manometer varying from 1.3 cm. to 6.15 cm. Observations were continued up to a total heating time of 93 hours, but had to be stopped when the fall in pressure became too large for the scale in the case of the more rapidly oxidized samples. The surface of the mercury remained satisfactorily clean.

The work described above has been carried out as part of the research program of the National Physical Laboratory, and this paper is published by permission of the Director of the Laboratory.

SUMMARY

In aging tests of rubber, the temperature and sometimes the oxygen pressure are raised much higher than in normal use; this has been necessary because the criteria of change usually chosen have been insensitive. The uptake of oxygen may be measured with considerable precision and, hence, the aging temperature may be reduced. An apparatus is described in which the absorption of oxygen by rubber is observable after an hour at 50° C; among the samples examined the hourly absorptions varied from 0.6 to 3.4 mg. per 100 grams of rubber. A manometer indicates differences in pressure between two similar bulbs placed side by side, one containing rubber and oxygen and the other containing air only. A formula is given to convert differences in the readings of the manometer to masses of oxygen absorbed.

SURFACE AREA AND PROPERTIES OF CARBON BLACK *

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One of the outstanding characteristics of carbon blacks is the large surface they possess by virtue of their extremely small particle size. In the past, many attempts have been made to measure this surface in an effort to correlate it with the properties carbon black is capable of imparting to various media in which it is dispersed.

Various methods of direct microscopic observations have been most widely employed^{10, 14, 15, 25}. While these direct methods are reliable for particles having diameters larger than 1000 Å., we have found that they are not reliable for particles with diameters smaller than 500 Å.

Since the majority of carbon blacks of commercial importance fall within this range, it must be concluded that surface areas calculated from diameters obtained by these methods are of doubtful significance. The electron microscope³ is an exception to the above general criticism of direct optical methods. Recent investigations² with this instrument have been remarkably successful. In addition to electron microscopy, other methods have been recently described for determining not only particle size and distribution, but also the direct determination of total surface area. The present paper deals with our attempts to apply certain of these methods a variety of commercial carbon blacks.

Hauser and his coworkers^{16, 17} used the supercentrifuge to determine particle-size distribution in a variety of finely divided substances. We have applied their method to a standard channel black dispersed in a rubber cement. Forty-five parts of black by weight were milled with 100 parts of rubber. This stock was then dissolved in xylene to give a final concentration of about 2×10^{-3} gram of black per cc. of suspension. After centrifuging and analysis, a distribution curve was obtained, with maxima in the region 300-400 Å., in fair agreement with the published electron microscopic value². Unfortunately the rubber in which the black was dispersed also fractionated along the sides of the centrifuge liner. This made it necessary to analyze each interval sample for rubber. Consequently several weeks were required to evaluate a single black. Because of these difficulties it did not appear that this method was particularly suited for a routine laboratory test.

We have also investigated²⁶ scattering in the near infra-red, as proposed by Gamble and Barnett¹³. Although this method is capable of distinguishing between coarse blacks (1500 Å.) and fine blacks (300 Å. diameter), it does not give quantitative results within the fine particle size region discussed above.

Emmett and Brunauer recently developed a method of determining total surface areas^{5, 6, 7} by measuring the volume of adsorbed gas required to form a unimolecular layer over the surface.²⁹ This is accomplished by measuring the adsorption isotherm of a suitable gas on the material under investigation at a temperature close to the boiling point of the gas employed. We applied this

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method to a variety of commercial carbon blacks, using nitrogen at -195.8°C as the adsorbate. The procedure is rapid and reproducible to at least 7 per cent. The areas so obtained are generally in excellent agreement with other accepted values.

Since this method does not involve the activity or specific nature of the surface, it is possible to evaluate the analytical and compounding properties of the carbon blacks strictly in terms of total surface.

ADSORPTION EXPERIMENTS

Apparatus.—The apparatus employed is the type commonly used in studying adsorption phenomena^{4, 11}. It consists of a water-jacketed gas buret, from which a known volume of gas is admitted to an adsorption cell of about 5-cc. capacity. The residual pressure in the cell after equilibrium is established is measured on an accurate mirror-scaled mercury manometer. All connecting tubing outside the bath on the adsorption side of the line is 1-mm. capillary. The line is evacuated through the usual mercury diffusion-oil pump system.

The nitrogen and oxygen were tank gases of 99.8 per cent purity. They were used without purification except for passage through traps at -78°C to remove traces of moisture. The helium, of 98 per cent purity, was freed from possible traces of hydrocarbon by passage through an active nut charcoal trap at -78° .

Procedure.—From 0.2 to 5 grams of sample, depending on the anticipated surface, were weighed into the adsorption cell. The cell was then sealed onto the line and evacuated to a flat gauge at 200°C . This usually required about 20-30 minutes. This procedure removed occluded air and physically adsorbed moisture. Most carbon blacks contain varying percentages of chemisorbed gases, chiefly oxygen. Volatile matter determination^{8, 24} before and after the above treatment showed that evacuation at 200° did not alter the amount of these chemisorbed gases on the black sample. After evacuation, the cell and sample were immersed in a liquid nitrogen bath, and the "dead space" was determined with helium. The helium was then pumped off and nitrogen admitted. By this procedure the adsorption isotherm was determined at pressure from 10 to 600 mm. Equilibrium was attained in about 10 minutes at the lower pressure. After completion of the unimolecular layer, up to 20 minutes was required for establishment of equilibrium.

In all cases V_m , the volume of gas at normal temperature and pressure required to form a monomolecular layer over the entire surface, was determined graphically from the expression⁷:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \frac{P}{P_0}$$

where V is the volume of nitrogen absorbed at the pressure, P , and the liquid nitrogen bath temperature of -195.8°C . P_0 , the vapor pressure of the nitrogen at this temperature, is 760 mm. C is a constant related exponentially to the difference between the heat of adsorption and liquefaction of the nitrogen. On plotting $P/V(P_0 - P)$ against P/P_0 , a straight line is obtained, the slope and intercept of which yield values of V_m and C . The total surface is then obtained by multiplying V_m by the appropriate factor. When nitrogen at -195.8° was used as the adsorbate, the value 4.38 M^2 per cc. adsorbed was employed. With oxygen at -183°C , the value 3.81 M^2 per cc. adsorbed⁶ was employed.

Typical isotherms for some of the carbons investigated are presented in Figure 1. Curve A is representative of a standard grade 6 rubber-reinforcing carbon black. After completion of this isotherm, the liquid nitrogen bath was removed, and the sample evacuated at room temperature. The bath was replaced and the isotherm repeated. The shaded circles on curve A are the values obtained on the second run. Consecutive runs with oxygen at -183°C on the same sample gave values of 108 and 109 M^2 per gram. The original nitrogen value for this sample was 110 M^2 per gram. After the two oxygen isotherms, the same sample was run with nitrogen and a value of 111 M^2 per gram obtained.

From these and other experiments, in which it was possible to recover the entire volume of adsorbed nitrogen by pumping at -78°C , it is apparent that

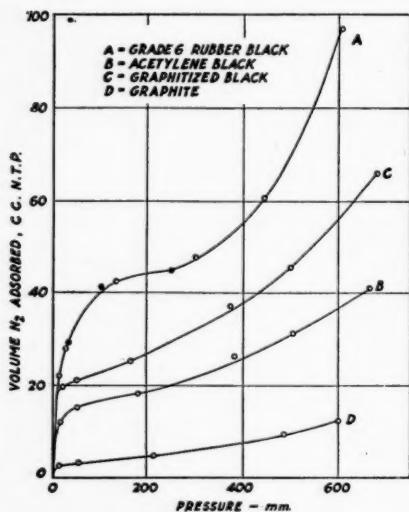


Fig. 1.—Typical isotherms for carbons investigated.

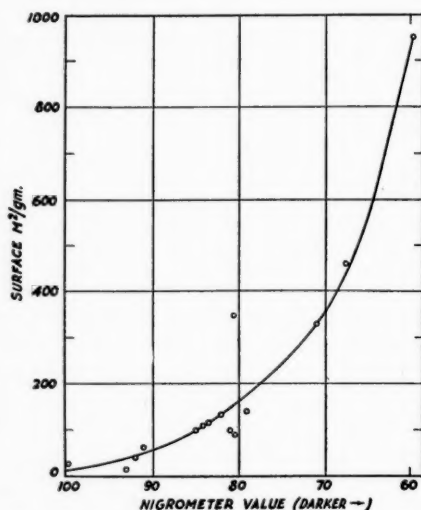


Fig. 2.—Relation between surface area and color intensity.

the adsorption forces involved are of the van der Waals type and, accordingly, the nature or activity of the surface is not involved.

ANALYTICAL PROPERTIES AND SURFACE AREAS

Table I presents the surface area and other analytical properties of a number of commercial carbons. Assuming a complete uniformity of particles and a density of 1.85, a diameter of 284 Å. is obtained from the surface area of a standard grade 6 rubber black. This is in excellent agreement with the published electron microscope value² of 280 Å. for this type of black.

From the surface area of acetylene black, a diameter of 533 Å. is calculated. A value of 510 Å. was recently obtained by electron microscope observation¹⁸. The excellent agreement between these independent values confirms the spherical shape and uniform size distribution of these pigments as disclosed by the electron microscope. It is only under these conditions that the calculation of diameters from surface area measurements is justified. The dark-field count diameter obtained with the optical dark-field microscope¹⁴ for the grade 6 black was found

to be 696 Å. The discrepancy with the value 284 Å. obtained from surface area measurements is not unexpected if one considers the limited resolving power of the optical microscope in this region. However, the dark-field diameters of grade 6 black and Mogul are nearly the same, yet the surface of Mogul black is three times that of grade 6. Other instances in Table I demonstrate the fact that dark-field diameters in this particle range are unreliable criteria of surface area.

The intensity of blackness of commercial carbons when incorporated in a suitable vehicle is a convenient method of comparison. By means of the nigrometer^{8, 19} the amount of light reflected by a 0.25-gram sample of black, hand-mulled in 3 cc. of standard No. 00 linseed oil varnish, can be readily measured on

TABLE I
SURFACE AREAS AND ANALYTICAL PROPERTIES

Sample	Area, M^2 per gram	Dark-field count (diam. in Å.)	Nigrometer value	Mg. iodine adsorbed per gram	Mg. D. P. G. adsorbed per gram	Volatile matter (%)
NONIMPINGEMENT BLACKS						
P-33	15	1570	93.0	53.3	2.5	0.47
Lampblack	28	—	99.7	41.9	3.2	1.34
Gastex	40	—	92.0	67.3	1.8	1.36
Acetylene black	64	—	91.0	104.0	8.0	0.30
IMPINGEMENT BLACKS						
Graphitized black "	90	—	80.2	130	1.0	0.17
Grade-9 rubber black	100	—	85.0	131	10.2	5.1
Grade-6 rubber black	114	696	83.4	136	11.8	5.5
Grade-3 rubber black	135	—	81.8	153	13.0	4.2
CK-3	100	740	81.0	131	7.4	3.0
Elf-20 ink black	110	650	83.8	130	11.0	5.5
Mogul ink black	350	661	80.5	266	47.0	11.3
Mogul calcined	450	—	78.0	562	8.3	0.0
Monarch-80 color black	140	—	80.0	165	12.1	4.5
Monarch-71 color black	330	550	71.0	435	23.2	4.3
Super-Carbovar color black	391	—	67.7	499	29.0	6.2
Carbolac-1 color black	947	250 ^b	58.8	765	192.0	16.7
Carbolac-1 calcined	990	—	62.1	1047	17.3	0.0
Nut charcoal	806	—	—	996	—	—

^a Grade 6 carbon black several hours at 2000° C.

^b From Gehman and Morris¹⁴.

an empirical scale. The greater the amount of reflected light, the grayer the carbon and the higher the value on the nigrometer scale. The intense blacks used as coloring pigments possess scales between 60 and 70; the rubber blacks range between 80 and 86. Blacks produced by non-impingement processes are quite gray and have high nigrometer readings of 90 or over. The degree of blackness or nigrometer values, determined as described above, are shown in Table I. The intensity of color is in general agreement with particle diameters, determined by dark-field count. Parkinson²² found a similar correlation with particle size, determined from centrifuge sedimentation curves. The relation between surface area and intensity of color is shown graphically in Figure 2.

In those cases in which the surface area and dark-field count diameters are in relative agreement, the correlation between intensity of color and surface area is good. In the case of high-volatile blacks, however, such as Mogul, the large

surface is not evident from either the dark-field count or the nigrometer value as ordinarily determined. That the discrepancy is not due to an effect of the high-volatile content on the surface area determination is evident from the data in Table I, which show that the high surface persists even after the volatile matter has been removed by calcination. However, a black of the Mogul type can be made to "develop" color in agreement with its high surface by grinding in a proper vehicle, whereas a black of the Elf 20 type will not develop additional color under similar conditions. These two blacks were hand-mulled in a standard No. 2 linseed oil varnish instead of the less viscous No. 00 commonly employed in these determinations. In this vehicle, Elf 20 had a color value of 90, and Mogul had a color of 84. After three passes through a tight three-roll ink mill the color value of the Elf 20 was unchanged, while the Mogul sample became much darker with a value of 78.

These and other results verify the surface area measurements of these two blacks, and it must be concluded that while two blacks may possess nearly identical average diameters as determined by dark-field count, the exposed surface may show a threefold variation. Whether this is due to a marked variation in particle size distribution or to some difference in the "topography" of the surface of each particle remains to be determined. Examination with the electron microscope may shed some light on the question.

The absorptive properties of carbon black have been the subject of considerable study,²³ due in part to the suggested correlation between these properties and the effect of black on cure^{1,28} in rubber vulcanization. Previous work on this subject has been complicated by the fact that independent values for total surface area have not been available. Since the present work places such values at our disposal, it is of interest to review these properties in the light of our results.

The iodine values given in Table I represents the number of milligrams of iodine adsorbed by 1 gram of black in equilibrium with a 0.5 *M* iodine solution. This final concentration is well out on the flat portion of the iodine isotherm. The relation between iodine adsorption and surface area is shown in Figure 3. With the exception of the two blacks having a volatile content over 10 per cent, a good linear relation exists between iodine adsorption and surface area. This is rather remarkable, considering the wide variety of carbons included in this study. The variation in surface activity between reinforcing channel black, graphitized channel black, and nut charcoal is undoubtedly large; yet the correlation between surface area and iodine adsorption is quite good, which indicates that iodine adsorption is independent of the specific nature of the carbon surface and is primarily a function of the total extent of surface.

From the present data, 130 mg. of iodine are associated with about 100 *M*² of surface, corresponding to a covering power of 32 square Å. per adsorbed iodine molecule and a diameter of 6.4 Å. The collision diameter of iodine from diffusion measurements²¹ is found to be 4.6 Å., in sufficient agreement with the approximate value obtained from the present measurements to indicate the possibility of formation of a monolayer of adsorbed iodine. It appears that when more than 10 per cent volatile matter is chemisorbed on the black, the iodine adsorption is reduced. That this is a specific effect of the volatile matter is evidenced by the fact that, when the volatile is removed by calcination, the iodine adsorption and surface areas are in much better agreement (Figure 3). The present data are not sufficient to indicate the reason for the decreased adsorption in these cases. Accordingly, in estimating surface areas from iodine adsorp-

tion, in the case of blacks of high volatile content (10 per cent and over), the result must be considered only as a minimum value.

The adsorption of diphenylguanidine (D. P. G.) by carbon black is widely used both as a control and guide to the curing properties of carbon blacks in the presence of organic accelerators^{1, 9}. The values in Table I were obtained by a technique similar to that of Amon and Estelow¹. They represent the number of milligrams of D. P. G. absorbed by 1 gram of black in equilibrium with a benzene solution of 0.01 *M*, final concentration. These data are plotted in Figure 4 against the surface area. It is difficult to observe a definite correlation between total surface and amount of diphenylguanidine adsorbed.

As Table I shows, some blacks with very high absorptive capacity, judged from surface area and iodine adsorption, actually possess low D. P. G. values.

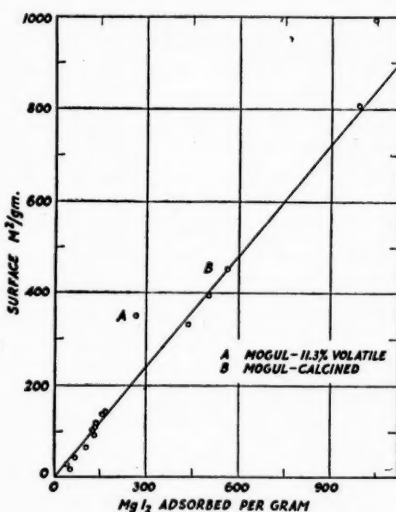


FIG. 3.—Relation between surface area and iodine adsorption.

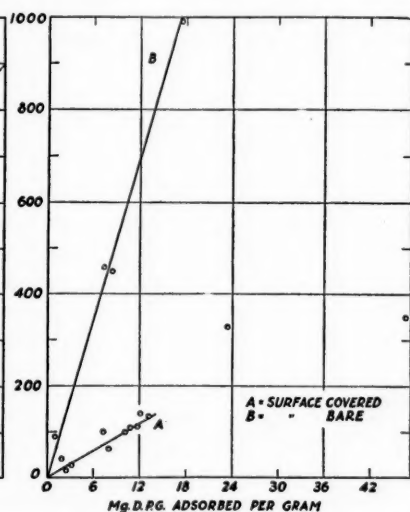


FIG. 4.—Relation between surface area and diphenylguanidine adsorption.

The blacks with low D. P. G. adsorption are generally found to be fast-curing in the presence of organic accelerators. Hence it is difficult to associate the retardation of cure displayed by most blacks in standard tread stock recipes with purely physical adsorption of the type displayed in the adsorption of iodine. Schoenfeld²³ arrived at similar conclusions.

It has been suggested^{1, 27} that D. P. G. adsorption is a function of the volatile content of the black. However, if the D. P. G. adsorption values of all the blacks presented in Table I are plotted against their corresponding volatile content, the suggested correlation is not evident. It must be realized, however, that these blacks vary greatly in surface area. The area generally increases more rapidly than the volatile content. For example, a grade-6 rubber black has a surface of 114 *M*² per gram and a volatile content of 5.5 per cent, whereas a Super-Carbovar black has a surface of 391 *M*² per gram and a volatile content of only 6.2 per cent. Assuming this chemisorbed gas to be located on the surface of the particle, it is evident that a wide variation exists in the relative extent of bare and oxygen-(volatile) covered surface per unit area. We find that a normally produced chan-

nel black with a surface of about $100 M^2$ per gram contains about 5 per cent volatile matter. This volatile matter, determined at $954^\circ C$, consists of about 80 per cent carbon monoxide and 20 per cent carbon dioxide. Five per cent volatile matter corresponds roughly to between 20 and 25 cc. of chemisorbed oxygen per gram of black. From our low-temperature oxygen isotherm, we find that 30 cc. of oxygen are required to form a physically adsorbed monolayer over the entire surface of 1 gram of such a black. In the absence of information as to the exact manner in which the chemisorbed oxygen is oriented on the carbon surface, it is not possible to interpret this rough correspondence too rigidly. However, it does appear probable that the surface of a black with an area of $100 M^2$ per gram and a volatile content of 5 per cent is almost completely covered with chemisorbed oxygen.

If the D.P.G. molecule is adsorbed primarily on oxygen and only weakly on the bare carbon surface, then D.P.G. adsorption will vary directly with surface area only as long as this surface is either covered with oxygen or is entirely bare. All the points falling on line *A* in Figure 4 correspond to those blacks in Table I possessing volatile-surface ratios in the order of 5 per cent per $100 M^2$ of surface, that is, with surfaces nearly covered with chemisorbed oxygen. A linear relation between D.P.G. adsorption and surface area exists, and from the slope we find about 10 mg. of D.P.G. adsorbed per $100 M^2$ of surface. Line *B* shows the same relation for the calcined and other low-volatile blacks, whose surfaces are assumed to be nearly bare of chemisorbed oxygen. The adsorption here is very weak, only 1.7 mg. of D.P.G. being adsorbed per $100 M^2$ of surface. We have not been able to detect a significant temperature coefficient for either the rate or the adsorption equilibrium; accordingly, with our present data it is not possible to describe the manner in which the highly polar D.P.G. molecule is associated with either the bare or oxygen-covered surface. While the polarity of the surface is of prime importance in this phenomenon, we do not feel that it is essential or clarifying to consider the volatile matter as adsorbed organic acids²³. It is hoped that further experiments now in progress will permit a more accurate interpretation of this process, a phenomenon which is evidently closely related to retardation of cure by carbon black in accelerated rubber stocks.

SURFACE AREA AND RUBBER REINFORCEMENT

The reinforcing ability of the commercial carbons given in Table I appears to increase in a very general manner with surface area. Similar conclusions have been deduced by other workers from particle size studies^{10, 22}. The exceptions to this trend, however, indicate that reinforcement cannot be described as a function of a single variable. In addition to possessing a large surface, it is essential that this surface be capable of being exposed to the compounding vehicle. Thus, although active charcoal has an extremely high measured surface area, its lack of reinforcing properties is due in part to its inability to disperse. Consequently, in judging reinforcement from surface area, such porous materials must be ruled out.

A third variable, which is not so readily evident as the above, is the activity or state of the surface. The occurrence of association between rubber hydrocarbon and black surface is of major importance, and is probably one of the essential differences between an inert and reinforcing pigment. This property is most strikingly brought out in the case of graphitized carbon black and grade-6 rubber

black. The graphitized black was prepared by heating grade-6 channel black for 10 hours at 2000° C in an induction furnace. Surface area measurements indicate that this treatment does not greatly alter the extent of available surface. However, the properties of the material in rubber are decidedly inferior to those of the original grade-6 black. To reduce cure effects, these two blacks were compared in the following simple litharge recipe:

Smoked sheet	100	Sublimed litharge	10
Black	40	Pine tar	2
Sulfur	4		

Examination of the compounded stock showed good dispersion in each case. The usual laboratory rubber tests were then performed on each stock, and the results are presented in Table II. The graphitized black shows a definite loss in those properties commonly associated with a good reinforcing black. Since the total

TABLE II
RESULTS OF LABORATORY RUBBER TESTS

Black	Cure (minutes)	400% modulus (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elonga- tion (%)	T-50 test (° C)
Graphitized	10	600	3400	770	+ 7.5
Grade-6	10	1100	3350	690	+ 6.5
Graphitized	20	700	4100	770	+ 3.3
Grade-6	20	1530	4450	680	- 0.1
Graphitized	30 ^a	780	4500	760	- 4.7
Grade-6	30	2150	4900	650	- 8.3
Graphitized	40	880	4750	760	- 10.9
Grade-6	40	2550	4800	600	- 16.5

^a At 30-minute cure, the wear resistance of graphitized black was 63 per cent of grade-6, according to the Williams abrasion test.

surface of the two blacks is almost the same, it seems plausible that the activity per unit area is quite different. This is not surprising in view of the extended heat treatment the graphitized black received. To estimate the relative activity of the two surfaces, we first considered the heat of adsorption for the first monolayer of nitrogen, as determined from their low-temperature adsorption isotherms⁷. For graphitized black, we obtain the value 2530 calories, compared to 2170 for grade-6 black. These values are identical within experimental error.

Similar relative values were obtained by determining the heat of wetting with benzene. These results indicate no essential differences in the state of the surface of these blacks. However, these measurements refer in each case to purely physical adsorption involving only van der Waals forces. If, on the other hand, the forces acting between rubber and carbon surfaces are primary chemical forces, they would not be apparent under the above conditions. Such forces would be evident only in case the adsorption was of the activated type. The adsorption of oxygen by carbon at elevated temperatures falls into this category²⁰. Consequently, if our assumption as to the nature of the forces involved in reinforcement is correct, we would anticipate a correlation between the rate of oxygen adsorption and rubber compounding properties. At 370° C and an initial pres-

sure of 270 mm., the amount of oxygen adsorbed per gram of black during the first 10 minutes of reaction is as follows:

Sample	Oxygen adsorbed (cc.)	Area (M ² per g.)
Graphitized	0.00	90
Grade-6	1.69	114

From these results a definite increase in the activity of the surface per unit area is evident, in accord with the relative values of these pigments as reinforcing agents. Although the kinetics of the above reaction have not been defined with sufficient clarity to warrant further exposition at present, preliminary studies of the temperature dependence indicate that the activation energy decreases with each of the blacks as written above.

Although the present data are far from complete, they are sufficient to indicate the importance of extent and activity of surface in determining the properties of carbon black. Further application of the methods discussed here should enable us to describe these variables more completely, and permit a more accurate estimation of the compounding properties of carbon black.

SUMMARY

The surface areas of a number of commercial carbon blacks have been determined by the low-temperature adsorption isotherm technique. Thermal decomposition and other nonimpingement type blacks possess areas of 15 to 64 M² per gram. Channel blacks commonly employed as reinforcing agents in rubber have areas around 100 M² per gram. Ink and color blacks range from 100 to nearly 1000 M² per gram. The color values of these carbons increase with surface area. The relation of iodine and diphenylguanidine adsorption to surface area has also been studied. Iodine adsorption is a direct function of surface area and, with the exception of certain high-volatile blacks, may be used as a direct measure of total surface. The adsorption of diphenylguanidine depends much more strongly on the volatile content of the black rather than its total surface. While rubber reinforcement depends in a general manner on surface area, certain blacks of nearly identical surface vary widely in the properties they impart to compounded rubber. That the state of the surface is probably of equal importance is indicated by the fact that the activity of the surface, as judged by relative ease of oxidation, may vary widely in blacks of equal area.

ACKNOWLEDGMENT

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INFLUENCE OF MOISTURE CONTENT OF CARBON BLACK ON RUBBER PROPERTIES *

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The large quantity of carbon black used in rubber tread stocks, and the tendency of blacks of this type to adsorb an appreciable amount of water vapor, bringing up the question of the influence of the adsorbed water vapor on the properties of the resultant stock. Although other compounds present can also adsorb

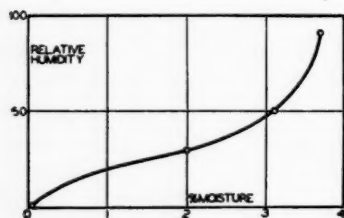


FIG. 1.—Water vapor adsorption isotherm at 27° C.

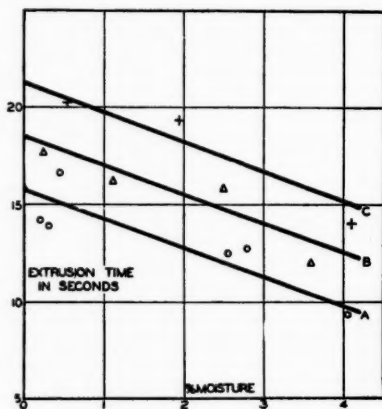


FIG. 2.—Effect of moisture on extrusion time of carbon black-rubber master batch.

water vapor, only carbon black is capable of carrying appreciable quantities into a tread stock.

The following series of experiments was conducted chiefly with the purpose of determining the extent to which this moisture affects the accuracy of testing carbon black, and thus to remove one of the uncertainties which enter into the evaluation of carbon black in rubber.

In Figure 1 a water vapor adsorption isotherm at 27° C is shown for the carbon black which was used as a standard in most of the experiments³. This black was the slow-curing small-particle type, had a volatile content of 5.1 per cent⁴, and diphenyl guanidine adsorption of 47.5². Figure 1 indicates that a change in humidity of only 10 per cent can change the moisture content of the black as much as 1 per cent. Thus small changes in atmospheric humidity can alter the moisture content of the black appreciably. The maximum amount of water vapor adsorbed by this black is about 4 per cent by weight. In those ex-

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periments, in which moisture contents higher than 4.2 per cent are reported, the blacks were allowed to adsorb liquid water. In no case, however, was liquid water used in preparing blacks of moisture contents less than 4.2 per cent.

EXTRUSION RESULTS

The very pronounced effect of moisture on the extrusion time of a carbon black-rubber master batch containing 40 per cent carbon black by weight is shown in Figure 2. A Firestone plastometer was used in all extrusion experiments, at a diaphragm pressure of 18 pounds and a thermostat temperature of 190° F. The three curves are for three different grades of rubber carbon black. Particularly in the case of blacks *A* and *B*, an **S**-shaped curve fits the experimental points more closely than the straight lines. However, in view of the limits of accuracy of the plastometer measurements, it was felt advisable to await additional evidence before deciding on the exact nature of the moisture content-extrusion function.

Figure 3 shows the dependence of extrusion time of an uncured tread stock on moisture content of the carbon black. The tread stock used in this and the following experiments contained by weight:

Smoked sheet	100
Standard carbon black.....	50.5
Zinc oxide	7.85
Stearite	3.30
Sulfur	2.81
Mercaptobenzothiazole	0.743
Total	165.2

The three sets of points in Figure 3 correspond to carbon black run in three separate master batches of the above formula.

Although the presence of moisture on the carbon black decreases the carbon loading, experiments have shown that the difference in loading between 0 and 4 per cent moisture content produces no change in extrusion time within the limits of error of the plastometer. For example, the dependence of extrusion time on loading for a carbon black-rubber master batch is as follows, where the carbon black contained 0.69 per cent moisture:

Loading (% by weight of carbon black in master batch)	Extrusion time, (seconds)
39.....	14.8
40.....	13.8
41.....	15.0

It was thought possible that the large change in extrusion time might be accounted for by the effect of moisture content on the completeness of dispersion of the carbon black. However, under the conditions of our experiments, no differences in the dispersion could be detected by comparing the sheen¹ of freshly torn surfaces of the various stocks. Furthermore, if changes in degree of dispersion were the cause of these large changes in extrusion, it would be logical to expect corresponding changes in tensile and modulus. As shown below, this is not the case.

Schoenfeld and Allen⁵ published results which indicate that the degree of dispersion of carbon black reaches a maximum when the black contains about 1 to 2 per cent water. This apparent disagreement with the present observations is probably due to the more intense mixing which our stocks received. The degree of dispersion produced by a 12-inch laboratory mill is so nearly perfect that differences in dispersibility produced by moisture changes are too small to detect. In any case, the extrusion-moisture content curves show no relation to the dispersibility-moisture curve of Schoenfeld and Allen.

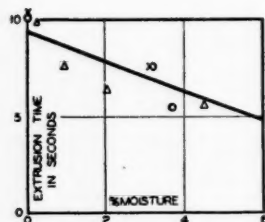


FIG. 3.—Dependence of extrusion time of uncured tread stock on moisture content of carbon black.

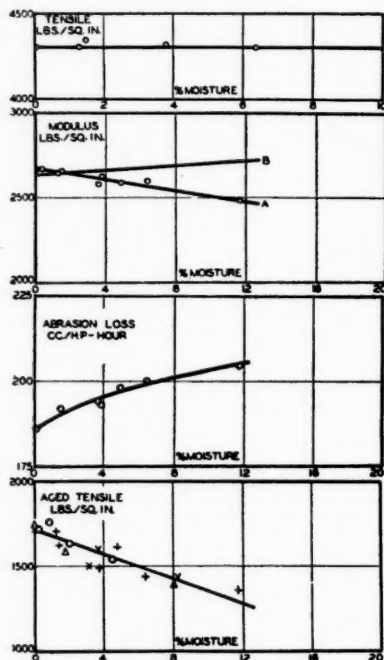


FIG. 4.—Effect of moisture content of carbon black on properties of cured rubber.

PROPERTIES OF CURED RUBBER

In Figure 4 the effects of moisture content of the carbon black on tensile strength, modulus at 400 per cent, abrasion loss, and aged tensile strength are shown. The data in all cases are for the optimum cure. In the three upper graphs, results for only one series of experiments are given; however, three check experiments gave essentially the same results.

Tensile strength at break point shows no trend, within the limits of accuracy of the experiment. In some of the check experiments, a tendency for the tensile measurements to scatter, particularly at higher moisture contents, was observed. Curve A shows that modulus at 400 per cent elongation decreases slightly with increasing moisture content. Again, more scattering was noticeable in some of the other experiments than in the one shown. However, the downward trend was present in all cases. If a correction is applied for the change in loading, cor-

rected curve, B , increases slowly with the moisture content. This increase is probably within the limits of error involved.

A du Pont abrader was used for the abrasion loss experiments, and the results are calculated in cubic centimeters lost per horsepower-hour (see Figure 4). The change in abrasion loss with increasing moisture content is in the same direction, as would be expected from the corresponding decrease in loading.

Aging tests were made in a Geer oven. Samples were aged for 4 days at 85° C. The tensile strength at rupture of the aged sample decreases about 20 per cent over the range 0 to 8 per cent moisture. The four series of points shown in Figure 4 are for four separate batches made up on the standard formula, but milled and aged at different times. The cure selected for aging tests was in each case the cure which corresponded to the maximum value for unaged tensile at rupture. This optimum cure time varied from about 65 minutes for the stock containing dry black to 55 minutes for the stock containing black of the highest water content used (11.7 per cent). As shown in the top graph of Figure 4, the tensile strengths of the unaged stocks showed no trend with increasing moisture content. The actual values of the unaged tensiles for the samples reported in the bottom graph of Figure 4 were within the limits 4300 ± 120 pounds.

It is worth noting that aging data taken at a definite cure—*e. g.*, 60 minutes—instead of at the optimum cure make the variation with moisture content more marked than is shown in the figure.

CONCLUSIONS

The moisture content of carbon black should be kept approximately constant if maximum accuracy in rubber testing is to be attained. In this laboratory we have found it convenient to equilibrate blacks at about 30 per cent humidity, under which condition most rubber channel blacks adsorb 1.5 to 2.0 per cent water. In the case of most of the properties of tread stocks, this precaution decreases the average deviation from the mean value in any series of experiments.

In the case of extrusion tests, the effect of adsorbed moisture is so great that the use of a standard moisture content, or at least the determination of moisture content at the same time as the black is milled for extrusion, is necessary if reproducible results are to be expected.

ACKNOWLEDGMENT

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